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ON CERTAIN DERIVATIVES OF THE 1,3,5-TRIIOD-2,4-DINITROBENZOL.

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This triioddinitrobenzol was described by Istrati and Georgescu,[1] in 1892, as they obtained it from their triiodbenzol, melting at 182° to 184°, made by heating together benzol, iodine, and sulphuric acid. They did not, however, determine its structure, which was done in 1900 by G. E. Behr and one of us,[2] who proved that it had the following constitution: $I_1,I_{1,3,5}.(NO_2)_{2,4}$. In 1901 Willgerodt and Arnold,[3] who apparently had overlooked the paper by Behr and one of us, in an extended paper on iodine compounds of benzol confirmed this result, proving its constitution in a different way.

In the paper just cited as issued from this laboratory in 1900, it was announced that the behavior of triioddinitrobenzol with various agents would be studied, and the present paper contains an account of the work done in this direction.

[1] Buletinul Soc. Sci. Fiz. Bucuresci, 1, 62 (1892).
[2] This JOURNAL, 26, 55 (1901).
[3] Ber. d. chem. Ges., 34, 3343 (1901).

This research belongs to a series undertaken for the purpose of studying the anomalous replacement of halogen atoms by hydrogen in aromatic compounds, and has added three more cases of the sort to the rather meager list at present known. Thus, triioddinitrobenzol is converted by hot sodic ethylate into dinitroresorcine diethyl ether, $C_6H_2(OC_2H_5)_2(NO_2)_2$, by the replacement of 2 atoms of iodine by ethoxy groups and 1 by hydrogen, in this respect resembling closely the corresponding reaction with tribromdinitrobenzol,[1] from which the same substance is obtained as one of the principal products. The melting-point of the dinitroresorcine diethyl ether obtained from tribromdinitrobenzol was 133°, that of our product from triioddinitrobenzol only 130°, and all our attempts failed to raise it above this point, but analysis proved that it was $C_6H_2(OC_2H_5)_2(NO_2)_2$. Dunlap and one of us[2] obtained a dinitroresorcine diethyl ether melting as low as 126° by the action of fuming nitric acid on dibromresorcine diethyl ether. It is possible that this diethyl ether melting at 126° is the other isomer $(OC_2H_5)_2$1.3.(NO_2)2.4 (the one melting at 133° has the constitution $(OC_2H_5)_2$1.3$(NO_2)_2$4.6), but we think it more probable that some clinging impurity caused the differences in melting-points, and that Dunlap's and our substances are identical with the one that melts at 133°. The point can be finally settled only by further experiment.

With sodic malonic ester, too, a monoioddinitrophenylmalonic ester, $C_6H_2I(NO_2)_2CH(COOC_2H_5)_2$, is formed, corresponding exactly to the $C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$, made in the same way from tribromdinitrobenzol,[3] but, whereas the bromdinitrophenylmalonic ester is the principal product of the reaction, the iod compound is formed only in secondary amount, the principal product being diioddinitrobenzol, formed by the replacement of 1 atom of iodine by hydrogen. It can be inferred from this that iodine is more easily replaced by hydrogen than bromine, since no dibromdinitrobenzol was observed among the products of the action of sodic malonic ester on tribromdinitrobenzol. This is not unexpected, as

[1] Jackson and Warren: This JOURNAL, 13, 170 (1891).
[2] *Ibid.*, 18, 122 (1890).
[3] *Ibid.*, 11, 94 (1889).

we have not found any case, as yet, in which chlorine has been replaced by hydrogen under the influence of an alcoholate or sodic malonic ester, and it was to be expected that the tendency toward such replacement should vary with the atomic weights.

With sodic methylate the behavior of the triioddinitrobenzol was peculiar, as the principal product was the triiodnitroanisol, $C_6HI_3NO_2OCH_3$, whereas with tribromdinitrobenzol the reaction runs as with the ethylate, the principal products being $C_6HBr(OCH_3)_3(NO_2)_2$ and $C_6H_2(OCH_3)_2(NO_2)_2$. A small amount of another substance was obtained, which, to judge from a single analysis, was $C_6HI(OCH_3)_3NO_2$, and therefore showed a similarity to the first of the brom compounds given above, but it was not obtained in sufficient quantity for proper characterization. A compound analogous to this triiodnitroanisol is formed from tribromdinitrobenzol by the action of sodic ethylate,[1] $C_6HBr_2NO_2OH$, but the amount is only a few per cent of the whole product, so that it was not detected until the experiment was tried on a large scale. On the other hand, the triiodnitroanisol must have been a principal product, as it was isolated from a complex mixture obtained from comparatively small quantities of the triioddinitrobenzol. Tribromtrinitrobenzol[2] shows similar replacements of nitro groups with sodic ethylate, forming tribromdinitrophenetol, $C_6Br_3(NO_2)_2OC_2H_5$, or tribromnitroresorcine diethyl ether, $C_6Br_2(NO_2)(OC_2H_5)_2$. The most probable explanation of this difference between tribromdinitrobenzol and triioddinitrobenzol is that iodine is held more strongly than bromine by the carbon of the benzol ring, so that the nitro group offers less resistance to replacement than the iodine, and this view is confirmed by the impression conveyed to our minds by these experiments that the triioddinitrobenzol was more sluggish in its behavior with reagents than the tribromdinitrobenzol, but this impression needs confirmation by careful comparative experiments before it can be accepted as proved.

[1] Jackson and Koch: This JOURNAL, **21**, 522 (1899).
[2] Jackson and Warren: *Ibid.*, **13**, 187 (1891).

In some of the experiments on the action of sodic malonic ester on the triioddinitrobenzol, a substance melting at 182° was obtained, which was proved to be an addition-compound of 2 molecules of diioddinitrobenzol with 1 of triioddinitrobenzol, $[C_6H_2I_2(NO_2)_2]_2C_6HI_3(NO_2)_2$. Its nature was established by the analysis of the compound, by breaking it up into its constituents by crystallizations from alcohol and benzol, and by making it from its constituents in alcoholic solution. A similar addition-compound, $[C_6HBr_2(NO_2)_2]_2C_6Br_4(NO_2)_2$, was obtained by Moore and one of us.[1]

It must be borne in mind that all the experiments described in this paper were tried with small quantities of substance, and, therefore, in no case have we identified all the products of a reaction. The compounds described may, however, fairly be considered the principal products in each case.

EXPERIMENTAL PART.

Preparation of Triioddinitrobenzol.

The triiodaniline used was prepared by a modification of the process of Michael and Norton,[2] as follows: Ten grams of freshly distilled aniline were dissolved in 500 cc. of strong hydrochloric acid and the whole diluted to 5 liters. A stream of air charged with the vapor of chloride of iodine (ICl) was then passed through this solution until 54 grams had been added. The flask containing the chloride of iodine was heated to 60°. The whole of the precipitate was used in making the triiodbenzol, both the light-brown one formed at first and the flocculent buff-colored precipitate deposited later. The filtrate was used to dissolve the aniline for the next operation. Our yield by this process amounted to 50 to 70 per cent and is therefore better than that obtained by Behr and one of us.[3]

The triiodbenzol was prepared from the triiodaniline by a slight modification of the method given in the paper just cited. Ten grams of the triiodaniline were boiled with 125 cc. of benzol and 25 cc. of alcohol, and disregarding the undissolved

[1] Ber. d. chem. Ges., **21**, 1707 (1888).
[2] *Ibid.*, **11**, 111 (1878). See also This JOURNAL, **26**, 55 (1901).
[3] This JOURNAL, **26**, 55 (1901).

portion, 5 cc. of commercial sulphuric acid were added, and after the mixture had cooled so that it was slightly warm, 5 grams of finely powdered sodic nitrite were added in small portions at a time, shaking the loosely corked flask after each addition. As soon as the evolution of nitrogen had slackened sufficiently the liquid was boiled for some time on the steam-bath, until a large part of the solvents had passed off. It was then allowed to stand over night, the deposit filtered out, and washed first with alcohol and afterwards with hot water. The yield with a gradual addition of the nitrite was better than when it was added all together, as recommended by Behr and one of us.[1]

The triiodbenzol was converted into triioddinitrobenzol by boiling 5 grams of it with 140 cc. of a mixture of 4 parts of fuming nitric acid (sp. gr. 1.5) and 1 part of common strong nitric acid for half an hour. The mixture, on cooling, deposited yellowish-white crystals, which were purified by crystallization from a mixture of benzol and ligroin.

Action of Sodic Methylate on Triioddinitrobenzol.

A preliminary experiment showed that sodic methylate in methyl alcoholic solution had but slight action in the cold, the solution being only light-yellow even after long standing, and the crude product melting at 195° to 200°. Accordingly, we carried on the reaction hot, as follows: Fifteen grams of triioddinitrobenzol were dissolved in 150 cc. of absolute methyl alcohol and mixed with a solution of sodic methylate made by treating 1.9 grams of sodium with methyl alcohol. This gives 3 molecules of sodic methylate for each molecule of the triioddinitrobenzol. The mixture was gently boiled for about eight hours in a flask with a return-condenser. It took on a brownish-yellow color almost at once, and this color did not alter as the reaction continued. The solvent was allowed to evaporate spontaneously at the end of the heating and the liquid poured off from the crystals after about half of it had evaporated. The residue left by the evaporation of the second half of the solvent, was washed thoroughly with water. The washings had a red color, indicating probably the salt of a

[1] This JOURNAL, **26**, 58 (1901).

phenol. The residue, insoluble in water, was crystallized from alcohol, when light-yellow clumps of radiating needles were obtained mixed with amorphous particles. The needles were separated mechanically and recrystallized from alcohol until they showed the constant melting-point 128°, when they were dried at 100° and analyzed with the following result:

I. 0.1621 gram substance gave, on combustion, 0.0920 gram CO_2 and 0.0219 gram H_2O.

II. 0.1362 gram substance gave, by the Carius method, 0.1818 gram AgI.

III. 0.2338 gram substance gave 0.3135 gram AgI.

	Calculated for $C_6HI_3NO_3OCH_3$.	Found. I.	II.	III.
C	15.82	15.48	....	....
H	0.75	1.50	....	....
I	71.73	....	72.16	72.46

The substance is therefore the triiodnitroanisol.

Properties of the Triiodnitroanisol, $C_6HI_3NO_3OCH_3$.—Crystallized from alcohol, it forms white or very light-yellow, slender prisms, terminated by a single plane at an oblique angle. It melts at 128°. It is freely soluble in benzol, ether, toluol, chloroform, acetone, or carbonic disulphide; moderately soluble in cold ethyl or methyl alcohol, freely soluble when hot; somewhat soluble in cold, more soluble in hot glacial acetic acid; insoluble in ligroin or water. Strong sulphuric acid dissolves it, giving a yellow solution; strong hydrochloric acid, or nitric acid, or sodic hydrate has no apparent action.

The less soluble portion of the product from the action of sodic methylate on triioddinitrobenzol yielded, after washing, recrystallization from alcohol, mechanical separation, and frequent recrystallizations from alcohol, a crystalline substance which melted between 253° and 256°. Unfortunately, the amount was too small to allow us to purify this body thoroughly, but an analysis of our best specimen gave the following results:

0.1635 gram substance gave, by the Carius method, 0.1122 gram AgI.

	Calculated for $C_6HI(OCH_3)_2NO_2$.	Found.
I	37.47	37.10

This analysis indicates that the substance was formed by the replacement of 2 atoms of iodine by methoxy groups in the triiodnitroanisol, which we have shown was a principal product of the reaction. This single analysis of a substance not certainly pure obviously needs confirmation before it can be accepted.

Action of Sodic Ethylate on Triioddinitrobenzol.

Ten grams of triioddinitrobenzol, dissolved in 75 cc. of absolute alcohol, were mixed with a solution of sodic ethylate prepared from 1.3 grams of sodium; that is, 3 molecules of ethylate were used to each molecule of the substituted benzol. A slight reaction took place in the cold, as shown by the appearance of a brownish-red color, but disregarding this, the mixture was boiled for fifteen minutes in a flask with a return-condenser. The dark-red solution was allowed to evaporate spontaneously, and the residue washed with water. The light-colored insoluble portion was recrystallized from alcohol until it showed the constant melting-point 130°, when it was dried at 100° and analyzed with the following result. It contained no iodine:

0.1382 gram substance gave, on combustion, 0.2365 gram CO_2 and 0.0627 gram H_2O.

	Calculated for $C_6H_2(NO_2)_2(OC_2H_5)_2$.	Found.
C	46.88	46.68
H	4.69	5.05

This proves that the substance is a dinitroresorcine diethyl ether, and we think it identical with that discovered by Warren and one of us,[1] although it melts at 130°, and the melting-point given in the paper cited is 133°. We explain this difference in melting-point by assuming the presence of an obstinately adhering impurity in our substance.

A small quantity of another body was also observed crystallizing in plates and melting near 200°, but we could not obtain enough of it for purification.

[1] This JOURNAL, 13, 170 (1891).

Action of Sodic Malonic Ester on Triioddinitrobenzol.

A number of different products were obtained from this reaction. Twenty-five grams of triioddinitrobenzol were dissolved in 300 cc. of absolute alcohol and mixed with 22 grams of malonic ester previously treated with the sodic ethylate made from 3.2 grams of sodium and 100 cc. of absolute alcohol. A red color appeared at once, but disregarding this, the mixture was boiled for five minutes in a flask with a return-condenser, and the product was then allowed to evaporate spontaneously. The residue was much less oily if the liquid had been acidified with hydrochloric acid, but in that case the salt of the substituted malonic ester could not be washed out directly with water, and the later purification was therefore more difficult. The residue was washed with water, and the portion insoluble in water, which was the principal product of the reaction, was washed several times with warm alcohol, which formed a dark-green solution and left a mass of yellow crystals. These were purified by crystallization from alcohol containing a little benzol until they showed the constant melting-point 160°, when they were dried at 100° and analyzed with the following result:

I. 0.2203 gram substance gave, on combustion, 0.1440 gram CO_2 and 0.0189 gram H_2O.

II. 0.2364 gram substance gave, by the Carius method, 0.2649 gram AgI.

III. 0.1781 gram substance gave 0.1991 gram AgI.

	Calculated for $C_6H_2I_3(NO_2)_2$.	Found. I.	II.	III.
C	17.15	17.83	....	....
H	0.47	0.96	....	....
I	60.47	....	60.57	60.43

The substance is therefore a diioddinitrobenzol formed from the triioddinitrobenzol by the replacement of 1 atom of iodine by 1 of hydrogen. To judge from the melting-point 160°, it is the same as the diioddinitrobenzol prepared by Istrati and Georgescu[1] by the action of nitric acid on their triiodbenzol melting at 83° to 84° (probably the vicinal isomer), since their dinitro body melts at 160° to 162°.

[1] Buletinul Soc. Sci. Fiz. Bucuresci, 1, 63.

Properties of Diioddinitrobenzol, $C_6H_1I_2(NO_2)_2$.—Crystallized from benzol containing a little alcohol it formed usually square-ended prisms arranged in groups formed by the union of the long sides of the prisms, so that the ends look like flights of steps. Less often it occurs in prisms terminated by several planes belonging apparently to the monoclinic system. From alcohol it crystallizes in long, slender needles very much branched, forming irregular, feather-like forms. It has a full yellow color and melts at 160°. It is freely soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; moderately soluble in cold ethyl or methyl alcohol, more so when hot; very slightly soluble in ligroin; insoluble in water. The best solvent for it is a mixture of alcohol and benzol. Strong sulphuric acid dissolves it slightly with a faint yellow color, but it seems to be unaffected by strong hydrochloric acid or nitric acid, or an aqueous solution of sodic hydrate.

Ioddinitrophenylmalonic Ester,
$C_6H_2I(NO_2)_2CH(COOC_2H_5)_2$.

In the preparation of the diioddinitrobenzol it was mentioned that the product insoluble in water was washed with warm alcohol. The dark-green washings, when allowed to evaporate spontaneously, left a mixture of white and yellow crystals. The latter were picked out mechanically as far as possible, and then recrystallized from ligroin until they showed the constant melting-point 83°, when they were dried *in vacuo* and analyzed with the following result:

I. 0.1821 gram substance gave, by the Carius method, 0.0946 gram AgI.

II. 0.1696 gram substance gave 0.0899 gram AgI.

	Calculated for $C_6H_2I(NO_2)_2CH(COOC_2H_5)_2$.	Found. I.	II.
I.	28.07	28.08	28.67

The substance is therefore ioddinitrophenylmalonic ester, formed by the replacement of 1 atom of iodine by the malonic ester radical and of a second by hydrogen.

Properties of Ioddinitrophenylmalonic Ester.—It crystallizes from alcohol in well-developed yellow, rhombic plates with each acute angle truncated by a plane, which look as if they belonged to the orthorhombic system. It melts at 83°, and is freely soluble in alcohol, ether, benzol, methyl alcohol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; moderately soluble in ligroin; insoluble in water. Ligroin is the best solvent for it. Strong hydrochloric acid has no apparent action on it. Strong nitric acid or sulphuric acid dissolves it, giving a yellow solution. Sodic hydrate gives with it a red solution of the sodium salt. In this respect it resembles most of the other nitrophenylmalonic esters known.

The colorless crystals which were mixed with the ioddinitrophenylmalonic ester, when first obtained, were found also in the mother-liquors from its recrystallization. They melted at about 73° and contained no iodine, but were not obtained in sufficient quantity for identification.

Addition-Compound of Diioddinitrobenzol and Triioddinitrobenzol, $[C_6H_2I_2(NO_2)_2]_2C_6I_3(NO_2)_3$.

In some of the experiments on the action of sodic malonic ester on triioddinitrobenzol still another compound was obtained, which was less soluble in cold alcohol even than the diioddinitrobenzol. It appeared in largest amount in the products of one reaction, which was carried on at ordinary temperatures. It was purified by repeated crystallization from hot alcohol, but we found it very hard to get it absolutely pure, as is shown by the following analyses of the substance dried at 100°:

I. 0.2660 gram substance gave, by the Carius method, 0.3119 gram AgI.

II. 0.2488 gram substance gave 0.2918 gram AgI.

	Calculated for $[C_6H_2I_2(NO_2)_2]_2C_6HI_3(NO_2)_3$.	Found. I.	Found. II.
I	64.14	63.37	63.40

These analyses indicate that the substance is an addition-compound of 2 molecules of the diioddinitrobenzol and 1 of the triioddinitrobenzol, but they are obviously insufficient to

establish its nature with certainty. The proof of its composition was given by its decomposition into its components and its synthesis from them. By crystallizing the substance from a mixture of alcohol and benzol, it was in time broken up into diioddinitrobenzol, melting at 160°, and triioddinitrobenzol, melting at 210°. These products were also recognized by their crystalline forms. Alcohol alone does not bring about this decomposition. To achieve its synthesis, a mixture of diioddinitrobenzol with triioddinitrobenzol, in the proportion of 2 molecules of the former to 1 of the latter, was boiled for two hours with alcohol in a flask with a return-condenser. Upon allowing the solids to crystallize two sorts of crystals were obtained, square-ended prisms like the addition-compound and needles like those of the diioddinitrobenzol, when crystallized from alcohol. The mother-liquors containing the needles were heated with a small additional amount of the triioddinitrobenzol, and after three recrystallizations a product was obtained which melted between 181° and 184°, and was identical in color and crystalline form with our addition-product. There can be no doubt, therefore, that our substance is really the compound

$$[C_6H_2I_2(NO_2)_2]_2C_6HI_3(NO_2)_2.$$

That it is not a mixture of the two components was shown by the fact that it gave, when crystallized from alcohol, crystals of only one sort, which differed from those of either of its components.

Properties of the Addition-Compound $[C_6H_2I_2(NO_2)_2]_2C_6HI_3(NO_2)_2$.—It crystallizes from alcohol in long, slender, square-ended prisms of a paler yellow than those of the diioddinitrobenzol, entirely different on the one hand from the long, slender, branching needles of the diioddinitrobenzol, and on the other from the thick needles in radiating bunches of the triioddinitrobenzol. It melts at 182° and is freely soluble in methyl alcohol, benzol, ether, chloroform, acetone, or carbonic disulphide; slightly soluble in cold, soluble in hot alcohol (difference from diioddinitrobenzol); slightly soluble in cold glacial acetic acid, freely soluble

when hot; slightly soluble in ligroin whether cold or hot. Alcohol is the best solvent for it. Benzol, even when mixed with alcohol, breaks it up into its components. It is not perceptibly affected by the three strong acids or an aqueous solution of sodic hydrate.

THE EXISTENCE OF HYDRATES IN SOLUTIONS OF CERTAIN NON-ELECTROLYTES AND THE NON-EXISTENCE OF HYDRATES IN SOLUTIONS OF ORGANIC ACIDS.

By Harry C. Jones and Frederick H. Getman[1] (Carnegie Research Assistant).

Having found that electrolytes in general form hydrates of greater or less complexity with water,[2] we naturally turned our attention to the non-electrolytes. These have been studied by the same general methods as were employed with the electrolytes, the conductivity method, of course, not being used.

In determining the freezing-point of dilute solutions, an ordinary Beckmann thermometer was used. For the more concentrated solutions, Beckmann thermometers having a range of 12° and 25° were employed. An alcohol thermometer was used to measure the freezing-points of the most concentrated solutions. The freezing-mixtures employed were salt and ice, calcium chloride and ice, or solid carbon dioxide and alcohol, depending on the concentration of the solution whose freezing-point was to be determined.

For the method of determining, from the experimental data, whether or not hydrates exist in solution, reference must be made to one of our earlier papers.[3] The specific gravities of the solutions were determined and used in the calculation of the composition of the hydrates in solution in a manner strictly analogous to that employed with the electrolytes.

In the following tables of "freezing-point measurements" m is the concentration in terms of gram-molecular normal, Δ

[1] This investigation was made possible by a grant from the Carnegie Institution, with which Dr. Getman was appointed a Research Assistant.

[2] Ztschr. phys. Chem., 46, 244; Phys. Rev., 18, 146; This Journal, 31, 303.

[3] *Loc. cit.*

is the lowering of the freezing-point observed; and $\frac{\Delta}{m}$ the molecular lowering of the freezing-point.

In the tables of "specific gravities," m is the concentration in terms of gram-molecular normal, $W_{Sol.}$ is the weight of 25 cc. of the solution; $W_{substance}$ is the weight of the substance in question in 25 cc. of the solution; W_{H_2O} is the weight of water in 25 cc. of the solution; and *correction* is the percentage difference between the amount of water in 1 liter of the solution and 1,000 grams of water.

In the tables of "hydrates," m is the concentration in terms of gram-molecular normal; L, the calculated molecular lowering for non-electrolytes; $\frac{\Delta}{m}$ the observed molecular lowering; L′ the molecular lowering corrected for specific gravities; m the number of gram-molecules of water combined with the substance at the concentration expressed by the abscissæ; $H = \frac{m}{m'}$ is the number of molecules of water combined with 1 molecule of the substance at the concentration in question.

We have worked with thirteen non-electrolytes, and the results obtained are given in the following tables. Care was taken in every case to test the purity of the substance used, and to purify the compound when the specimen, furnished in most cases by Kahlbaum, was not sufficiently pure.

Methyl Alcohol.

The results are given in Tables I. to III. A glance at Table I. will show a marked increase in the molecular lowering, $\frac{\Delta}{m}$, with increase in concentration. This would suggest at first sight that there is considerable hydration in the more concentrated solutions. Such, however, is not the case. When the observed molecular lowering is corrected for specific gravity, *i. e*, referred to 1,000 grams of the solvent, the observed lowering does not differ greatly from the calculated. This is seen by comparing column L′ with column L, Table III. At no concentration do we find as much as 1 molecule of water combined with every molecule of the alcohol.

The freezing-point data for methyl alcohol are plotted as a curve (Fig. I.). The abscissæ represent concentrations and

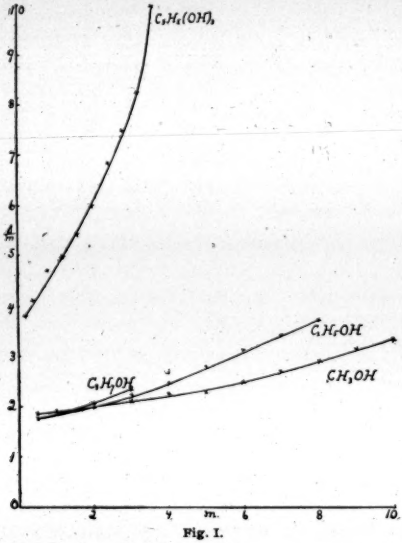

Fig. I.

the ordinates molecular lowering of the freezing-point.

Table I.—Freezing-point Measurements.

Methyl alcohol, $CH_4O = 32.04$.

m.	Δ.	$\frac{\Delta}{m}$.
0.5	0.935	1.87
1.0	1.898	1.90
2.0	....	....
3.0	6.440	2.15
4.0	9.130	2.28
5.0	11.500	2.30
6.0	15.000	2.50
7.0	19.000	2.71
8.0	23.500	2.94
9.0	28.500	3.17
10.0	33.500	3.35

Table II.—Specific Gravities.

m.	$W_{Sol.}$	W_{CH_4O}.	W_{H_2O}.	Correction. Per cent.
0.5	24.8825	0.4000	24.4825	2.07
1.0	24.8071	0.8000	24.0071	3.97
2.0	24.7032	1.6000	23.1032	7.89
3.0	24.5111	2.4000	22.1111	11.86
4.0	24.3773	3.2000	21.1773	15.29
5.0	24.2655	4.0000	20.2655	18.94
6.0	24.1013	4.8000	19.3013	22.79
7.0	24.0195	5.6000	18.4195	26.32
8.0	23.8966	6.4000	17.4966	30.01
9.0	23.7476	7.2000	16.5476	33.81
10.0	23.6050	8.0000	15.6050	37.58

Table III.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.	*m*.	H.
0.5	1.86	1.87	1.83	..	..
1.0	1.86	1.90	1.86	..	..
..	....	....	....	..	..
3.0	1.86	2.15	1.90	1.1	0.4
4.0	1.86	2.28	1.93	2.0	0.5
5.0	1.86	2.30	1.87	..	..
6.0	1.86	2.50	1.93	2.0	0.3
7.0	1.86	2.71	2.00	3.9	0.5
8.0	1.86	2.94	2.06	5.4	0.7
9.0	1.86	3.17	2.10	6.4	0.7
10.0	1.86	3.35	2.10	6.4	0.6

Ethyl Alcohol.

Results were obtained with ethyl alcohol which are of the same general character as those given by methyl alcohol. The freezing-points of the solutions of ethyl alcohol are, however, lower than those of methyl alcohol of the same concentrations. The corrections for specific gravities are larger for the ethyl alcohol, so that the amount of hydration shown by this substance is not very much greater than that shown by methyl alcohol.

The data for ethyl alcohol are recorded in Tables IV. to VI., and the freezing-point measurements are plotted in Fig. I. The magnitude of the hydration shown by ethyl alcohol is seen in Table VI. There is, of course, the possibility that

ethyl alcohol undergoes some polymerization in solution and that the true hydration is greater than would be indicated by these figures.

Table IV.—Freezing-point Measurements.

Ethyl alcohol, $C_2H_6O = 46.06$.

m.	Δ.	$\frac{\Delta}{m}$.
0.5	0.895	1.790
1.0	1.872	1.872
2.0	4.010	2.005
3.0	6.720	2.240
4.0	9.960	2.490
5.0	14.200	2.840
6.0	19.000	3.160
7.0	24.250	3.460
8.0	30.000	3.740

Table V.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_2H_6O}$.	W_{H_2O}.	Correction. Per cent.
0.5	24.8275	0.5750	24.2525	2.99
1.0	24.7147	1.1500	23.5647	5.74
2.0	24.5514	2.3100	22.2414	9.03
3.0	24.3845	3.4500	20.9345	16.26
4.0	24.2400	4.6200	19.6200	21.52
5.0	24.0891	5.7500	18.3391	26.65
6.0	23.8720	6.9000	16.9720	32.11
7.0	23.6930	8.0500	15.6430	37.43
8.0	23.4333	9.2400	14.1933	43.23

Table VI.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.	m.	H.
0.5	1.86	1.790	1.740	..	..
1.0	1.86	1.872	1.765	..	..
2.0	1.86	2.005	1.825	..	..
3.0	1.86	2.240	1.873	..	..
4.0	1.86	2.490	1.955	2.7	0.7
5.0	1.86	2.840	2.082	6.0	1.2
6.0	1.86	3.160	2.150	6.9	1.1
7.0	1.86	3.460	2.166	7.8	1.1
8.0	1.86	3.740	2.120	6.8	0.8

n-Propyl Alcohol.

Propyl alcohol gives lowerings of the freezing-point that differ markedly from those produced by methyl and ethyl alcohols. The molecular lowering increases with the concentration up to a certain point, passes through a maximum and then decreases (Table VII.). The corrected molecular lowering is smaller than the theoretical value, 1.86, at nearly all concentrations, and becomes very much smaller in the more concentrated solutions. Indeed, in a six-normal solution the corrected molecular lowering becomes less than half of the theoretical value. This is shown in Table IX.

The explanation of these results is to be found, undoubtedly, in the polymerization of the molecules of normal propyl alcohol, especially in concentrated solution. It is, therefore, impossible to say in such cases whether or not there is any hydration.

Table VII.—Freezing-point Measurements.

n-Propyl alcohol, C_3H_7OH.

m.	Δ.	$\frac{\Delta}{m}$.
0.5	0.890	1.78
1.0	1.900	1.90
2.0	4.160	2.08
3.0	7.100	2.37
4.0	8.820	2.20
5.0	9.450	1.89

Table VIII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_3H_7OH}$.	W_{H_2O}.	Correction. Per cent.
0.5	24.8348	0.7500	24.0848	3.66
1.0	24.6690	1.5000	23.1690	7.32
2.0	24.4770	3.0000	21.4770	14.09
3.0	24.2478	4.5000	19.7478	21.0
4.0	23.9394	6.0000	17.9394	28.24
5.0	23.5960	7.5000	16.0960	33.62
6.0	23.2411	9.0000	14.2411	43.04
7.0	22.8372	10.5000	12.3372	50.65

Table IX.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.
0.5	1.86	1.78	1.71
1.0	1.86	1.90	1.76
2.0	1.86	2.08	1.79
3.0	1.86	2.37	2.04
4.0	1.86	2.20	1.58
5.0	1.86	1.89	1.25
6.0	1.86	1.50	0.85

Acetone.

The freezing-point lowerings produced by acetone increase considerably with increase in the concentration of the solution, but the correction for specific gravity is unusually large (Table XI.). When the proper corrections are applied, the "true molecular lowerings" decrease with increase in the

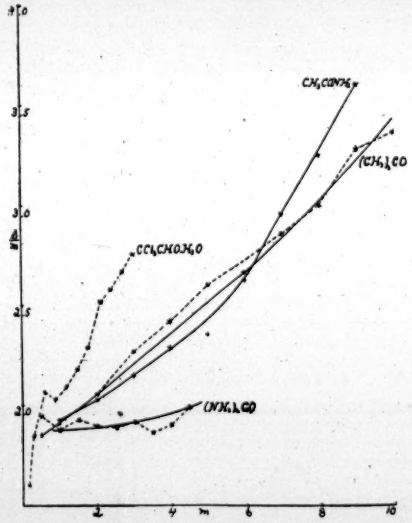

Fig. II.

concentration of the solutions. The experimental values at all concentrations studied are below the calculated value for a non-dissociated, non-polymerized substance, and at great concentrations the values found fall very much below the theoretical value (column L′, Table XII.).

This shows that the acetone undergoes polymerization in such solutions, the amount of the polymerization being a function of the concentration—increasing from the most dilute to the most concentrated solutions studied. The freezing-point curve is plotted in Fig. II.

Table X.—Freezing-point Measurements.

Acetone, $CH_3.CO.CH_3 = 58.06$.

m.	Δ.	$\frac{\Delta}{m}$.
0.5	0.930	1.860
1.0	1.919	1.919
2.0	4.110	2.055
3.0	6.800	2.270
4.0	9.700	2.420
5.0	13.000	2.600
6.0	16.000	2.670
7.0	20.000	2.86
8.0	24.000	3.00
9.0	29.560	3.28
10.0	33.75	3.37

Table XI.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_3H_6O}$.	W_{H_2O}.	Correction. Per cent.
0.5	24.8177	0.7250	24.0927	3.63
1.0	24.7292	1.4500	23.2792	6.88
2.0	24.5396	2.9000	21.6396	13.44
3.0	24.3129	4.3500	19.9629	20.15
4.0	24.1056	5.8000	18.3056	26.78
5.0	23.8278	7.2500	16.5778	33.69
6.0	23.5748	8.7000	14.8748	40.00
7.0	23.2513	10.1500	13.1013	47.59
8.0	22.9160	11.6000	11.3160	54.74
9.0	22.5212	13.0500	9.4712	62.12
10.0	22.0880	14.5000	7.4880	70.04

Table XII.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.
0.5	1.86	1.860	1.790
1.0	1.86	1.919	1.787
2.0	1.86	2.055	1.780
3.0	1.86	2.270	1.816
4.0	1.86	2.420	1.774
5.0	1.86	2.600	1.724
6.0	1.86	2.670	1.586
7.0	1.86	2.860	1.499
8.0	1.86	3.000	1.358
9.0	1.86	3.280	1.246
10.0	1.86	3.370	1.011

Acetamide.

While the value of $\frac{\Delta}{m}$ for acetamide increases rapidly with the concentration, the corrected molecular lowering, L', Table XV., does not change appreciably in magnitude. Indeed, the values found at the various dilutions do not differ appreciably from the theoretical value 1.86. This indicates that acetamide neither forms hydrates nor undergoes polymerization at any dilution.

There is, of course, the possibility that these influences are simultaneously operative, but in order that this should be true, we would have to assume that the magnitude of each of these influences was exactly equal at all concentrations, which is a highly improbable assumption. The freezing-point data for acetamide are plotted in Fig. II.

Table XIII.—Freezing-point Measurements.

Acetamide, $CH_3.CO.NH_2 = 59.09$.

m.	Δ.	$\frac{\Delta}{m}$.
0.4	0.782	1.93
1.0	1.930	1.93
2.0	4.050	2.03
3.0	6.440	2.15
4.0	9.150	2.29
5.0	11.800	2.36
6.0	15.800	2.63
7.0	20.750	2.96
8.0	26.000	3.25
9.0	32.500	3.61

Table XIV.—Specific Gravities.

m.	$W_{Sol.}$	$W_{CH_3CONH_2}$.	W_{H_2O}.	Correction. Per cent.
0.4	24.9502	0.5900	24.3602	2.56
1.0	25.0486	1.4750	23.5736	5.70
2.0	25.1446	2.9500	22.1946	11.22
3.0	25.2355	4.4250	20.8105	16.76
4.0	25.3858	5.9000	19.4858	22.06
5.0	25.4530	7.3750	18.0780	27.69
6.0	25.5606	8.8500	16.7106	33.16
7.0	25.6660	9.3250	16.3410	34.64
8.0	25.7861	11.8000	13.9861	44.06
9.0	25.8257	13.2750	12.5500	49.80

Table XV.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.
0.4	1.86	1.93	1.88
1.0	1.86	1.93	1.82
2.0	1.86	2.03	1.81
3.0	1.86	2.15	1.79
4.0	1.86	2.29	1.79
5.0	1.86	2.36	1.71
6.0	1.86	2.63	1.76
7.0	1.86	2.96	1.94
8.0	1.86	3.25	1.82
9.0	1.86	3.61	1.79

Urea.

The observed molecular depression produced by urea does not change appreciably with the concentration, as is seen in column $\frac{\Delta}{m}$, Table XVI. When these values are corrected for specific gravities, the true molecular lowerings decrease quite markedly with increase in the concentration of the solutions. This is seen in column L', Table XVIII.

Here, again, we have considerable polymerization, and the amount of the polymerization increases with the concentration of the solutions.

The curve for urea is given in Fig. II.

Table XVI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.5	0.975	1.95
1.0	1.878	1.88
1.5	2.900	1.93
2.0	3.800	1.90
2.5	4.724	1.89
3.0	5.767	1.92
3.5	6.555	1.87
4.0	7.625	1.91
4.5	8.975	1.99

Table XVII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Urea.}$	W_{H_2O}	Correction. Per cent.
0.5	25.1409	0.7500	24.3909	2.44
1.0	25.3258	1.5000	23.8258	4.70
1.5	25.4996	2.2500	23.2496	7.00
2.0	25.7206	3.0000	22.7206	9.12
2.5	25.8933	3.7500	22.1433	11.43
3.0	26.1085	4.5000	21.6085	13.57
3.5	26.2992	5.2500	21.0492	15.80
4.0	26.4785	6.0000	20.4785	18.09
4.5	26.6456	6.7500	19.8956	20.42

Table XVIII.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.
0.5	1.86	1.95	1.90
1.0	1.86	1.88	1.80
1.5	1.86	1.93	1.75
2.0	1.86	1.90	1.73
2.5	1.86	1.89	1.67
3.0	1.86	1.92	1.66
3.5	1.86	1.87	1.57
4.0	1.86	1.91	1.57
4.5	1.86	1.99	1.58

Chloral Hydrate.

The freezing-point curve for chloral hydrate (Fig. II.) is somewhat remarkable. It shows one or two well-defined breaks, the meaning of which is not apparent. While the observed molecular lowering increases quite markedly with

the concentration (Table XIX.) the corrected molecular lowering, L′, Table XXI., shows only slight increase as the concentration of the solution increases. The true molecular lowering produced by chloral hydrate is never much larger than the theoretical value, and, therefore, this substance does not show any marked hydration at any of the dilutions with which we worked.

Table XIX.—Freezing-point Measurements.

Chloral hydrate, $CCl_3.COH.H_2O = 165.38$.

m.	Δ.	$\frac{\Delta}{m}$.
0.15	0.260	1.73
0.30	0.556	1.85
0.60	1.241	2.07
0.90	1.825	2.03
1.2	2.505	2.09
1.5	3.274	2.18
1.8	4.176	2.29
2.1	5.200	2.52
2.4	6.170	2.58
2.7	7.200	2.67
3.0	8.280	2.76

Table XX.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{CCl_3.COH.H_2O}$.	W_{H_2O}.	Correction. Per cent.
0.15	25.2450	0.6202	24.6248	1.50
0.3	25.5002	1.2405	24.2597	2.96
0.6	26.0785	2.4810	23.5975	5.61
0.9	26.5458	3.7215	22.8243	8.70
1.2	27.1197	4.9620	22.1577	11.37
1.5	27.6235	6.1025	21.5210	13.92
1.8	28.1998	7.4430	20.7568	16.97
2.1	28.7492	8.6835	20.0657	19.74
2.4	29.1582	9.9240	19.2342	23.06
2.7	29.3230	11.1645	18.1585	27.37
3.0	30.2896	12.4050	17.8846	28.46

Table XXI.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L′.
0.15	1.86	1.73	1.70
0.3	1.86	1.85	1.80
0.6	1.86	2.07	1.95
0.9	1.86	2.03	1.85
1.2	1.86	2.09	1.86
1.5	1.86	2.18	1.88
1.8	1.86	2.29	1.90
2.1	1.86	2.52	2.02
2.4	1.86	2.58	2.00
2.7	1.86	2.67	1.95
3.0	1.86	2.76	1.97

Glycerol.

The case of glycerol among the non-electrolytes is particularly interesting, in that it shows very marked hydration. This would be indicated by the large molecular lowerings recorded in Table XXII., and curve Fig. I., and is obvious from the large values of the corrected molecular lowerings, L′, in Table XXIV.

The degree of the hydration is shown in column H, Table XXIV. We are impressed, first, by the large number of molecules of water combined with 1 molecule of the glycerol, and, second, by the fact that the complexity of the hydrate increases regularly from the most dilute to the most concentrated solution investigated. The hydrate curve for glycerol is given in Fig. IV., where the abscissae represent concentrations and the ordinates the number of molecules of water combined with 1 molecule of glycerol.

Table XXII.—Freezing-point Measurements.

Glycerol, $C_3H_5(OH)_3 = 92.08$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.76	3.80
0.4	1.65	4.12
0.8	3.75	4.70
1.2	6.00	5.00
1.6	8.70	5.44
2.0	12.00	6.00
2.4	16.50	6.87
2.8	21.00	7.50
3.2	26.50	8.28
3.6	36.00	10.00

Table XXIII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_3H_5(OH)_3}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.2010	0.4600	24.7410	1.04
0.4	25.3351	0.9200	24.4151	2.34
0.8	25.8055	1.8400	23.9655	4.14
1.2	26.2256	2.7600	23.4656	6.14
1.6	26.6665	3.6800	22.9865	8.05
2.0	27.0463	4.6000	22.4463	10.21
2.4	27.4440	5.5200	21.9240	12.30
2.8	27.8344	6.4400	21.3944	14.42
3.2	28.1801	7.3600	20.8201	16.72
2.6	28.5580	8.2800	20.2780	18.89

Table XXIV.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.	M.	H.
0.2	1.86	3.80	3.76	28.0	140.0
0.4	1.86	4.12	4.03	30.1	75.2
0.8	1.86	4.70	4.51	32.6	40.8
1.2	1.86	5.00	4.70	33.5	28.0
1.6	1.86	5.44	5.00	34.9	21.8
2.0	1.86	6.00	5.40	36.4	18.2
2.4	1.86	6.87	6.03	38.6	16.1
2.8	1.86	7.50	6.42	39.4	10.5
3.2	1.86	8.28	7.30	41.4	12.9
3.6	1.86	10.00	8.11	42.8	11.9

Glucose.

Turning to the carbohydrates, we find very little hydration shown by glucose. The freezing-point lowerings produced by glucose are plotted in Fig. III. A comparison of the corrected molecular lowerings, L', Table XXVII., with the theoretical molecular lowering, L, of the same table, will show that in the more concentrated solutions the experimental value is slightly greater than the theoretical. The difference is so small that the amount of hydration shown by this substance is very slight indeed.

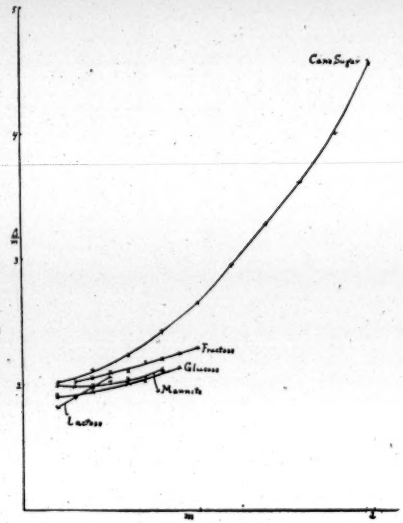

Fig. III.

Table XXV.—Freezing-point Measurements.

Glucose, $C_6H_{12}O_6 = 180$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.380	1.91
0.3	0.574	1.91
0.4	0.780	1.95
0.5	1.023	2.04
0.6	1.220	2.03
0.7	1.430	2.04
0.8	1.690	2.11
0.9	1.930	2.14

Table XXVI.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_6H_{12}O_6}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.2810	0.9000	24.3810	2.48
0.3	25.4412	1.3500	24.0912	3.64
0.4	25.6245	1.8000	23.8245	4.70
0.5	25.8192	2.2500	23.5689	5.72
0.6	25.9539	2.7000	23.2539	6.98
0.7	26.1361	3.1500	22.9861	8.06
0.8	26.2819	3.6000	22.6819	9.27
0.9	26.4712	4.0500	22.4212	10.32
1.0	26.5827	4.5000	22.0827	11.67

Table XXVII.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.
0.2	1.86	1.91	1.86
0.3	1.86	1.91	1.85
0.4	1.86	1.95	1.86
0.5	1.86	2.04	1.92
0.6	1.86	2.03	1.89
0.7	1.86	2.04	1.88
0.8	1.86	2.11	1.91
0.9	1.86	2.14	1.93

Fructose.

Fructose, unlike glucose, shows considerable hydration, especially in the more dilute solutions. The complexity of the hydrates is seen in column H, Table XXX. Fructose, like glycerol, forms hydrates which are more and more complex the more dilute the solution. The non-electrolytes that form hydrates in solution thus differ from those of the electrolytes. The complexity of the latter reaches a maximum at a definite concentration and then becomes less and less, both with increase in the dilution and with increase in the concentration of the solutions. This is probably connected in some way with the fact that with the non-electrolytes we have only molecules present, while in solutions of electrolytes we have both molecules and ions present. The curve of hydrates for fructose is given in Fig. IV.

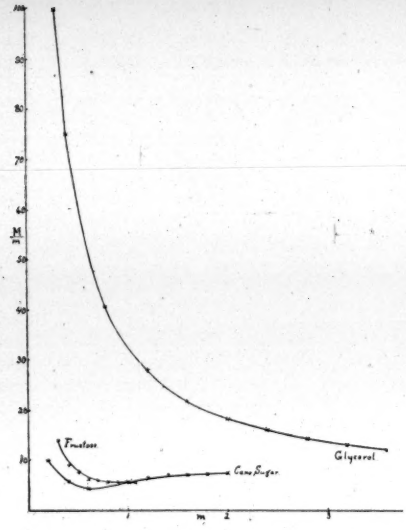

Fig. IV.

Table XXVIII.—Freezing-point Measurements.

Fructose, $C_6H_{12}O_6 = 180$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.384	1.92
0.3	0.610	2.03
0.4	0.830	2.07
0.5	1.054	2.11
0.6	1.265	2.11
0.7	1.535	2.19
0.8	1.765	2.21
0.9	2.033	2.26
1.0	2.300	2.30

Table XXIX.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_6H_{12}O_6}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.3519	0.9000	24.4519	2.19
0.3	25.5315	1.3500	24.1815	3.27
0.4	25.7306	1.8000	23.9306	4.28
0.5	25.8911	2.2500	23.6411	5.44
0.6	26.0845	2.7000	23.3845	6.46
0.7	26.1856	3.1500	23.0356	7.86
0.8	26.4080	3.6000	22.8080	8.77
0.9	26.5790	4.0500	22.5290	8.88
1.0	26.7699	4.5000	22.2699	10.92

Table XXX.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.2	1.86	1.92	1.88	..	...
0.3	1.86	2.03	1.96	2.8	14.0
0.4	1.86	2.07	1.98	3.7	9.2
0.5	1.86	2.11	2.00	3.9	7.8
0.6	1.86	2.11	1.99	3.6	6.0
0.7	1.86	2.19	2.02	4.4	6.3
0.8	1.86	2.21	2.02	4.4	5.5
0.9	1.86	2.26	2.04	5.0	5.5
1.0	1.86	2.30	2.05	5.3	5.3

Mannite.

Mannite, on the other hand, has very little power to combine with water at any of the dilutions at which work could be done. On account of its comparatively slight solubility, however, we could not work at any considerable concentration.

A comparison of column L′ with column L, Table XXXIII., shows that this substance gives molecular lowerings of the freezing-point of water that are only slightly greater than the theorerical lowering. Further, there is no apparent regularity in the difference between the value found and the calculated value. The amount of hydration is so slight that it was not even calculated. The values of $\frac{\Delta}{m}$, Table XXXI., for this substance are plotted in Fig. III.

Table XXXI.—Freezing-point Measurements.

Mannite, $C_6H_{10}O_6 = 182$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.400	2.00
0.3	0.600	2.00
0.4	0.800	2.00
0.5	1.033	2.07
0.6	1.234	2.06
0.7	1.440	2.06
0.8	1.700	2.13

Table XXXII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_6H_{14}O_6}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.2628	0.9100	24.3528	2.59
0.3	25.4320	1.3650	24.0670	3.73
0.4	25.5747	1.8200	23.7547	4.98
0.5	25.7431	2.2750	23.4681	6.13
0.6	25.9235	2.7300	23.1935	7.23
0.7	26.0495	3.2350	22.8145	8.74
0.8	26.1478	3.6400	22.5078	9.97

Table XXXIII.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.
0.2	1.86	2.00	1.95
0.3	1.86	2.00	1.93
0.4	1.86	2.00	1.90
0.5	1.86	2.07	1.95
0.6	1.86	2.06	1.91
0.7	1.86	2.06	1.88
0.8	1.86	2.13	1.92

Lactose.

Lactose not only shows no hydration, but the corrected molecular lowerings, L', Table XXXVI., are less than the theoretical value 1.86. This would indicate a certain amount of polymerization in the solutions. On account of the limited solubility of lactose we could not study concentrations greater than half-normal.

The molecular lowerings $\frac{\Delta}{m}$, Table XXXIV., found for lactose are plotted in a curve, Fig. III.

Table XXXIV.—Freezing-point Measurements.

Lactose, $C_{12}H_{22}O_{11} = 342.22$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.364	1.82
0.3	0.574	1.91
0.4	0.792	1.98
0.5	1.030	2.06

Table XXXV.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_{12}H_{22}O_{11}}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.5793	1.7100	23.8693	4.52
0.3	25.8796	2.5650	23.3146	6.74
0.4	26.1958	3.4200	22.7758	8.89
0.5	26.5176	4.2750	22.2426	11.03

Table XXXVI.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.
0.2	1.86	1.82	1.74
0.3	1.86	1.91	1.78
0.4	1.86	1.98	1.80
0.5	1.86	2.06	1.83

Cane-Sugar.

It has been known for some time that cane-sugar, in concentrated solutions, gives molecular lowerings that are considerably greater than the theoretical value. Arrhenius[1] established this fact in connection with his early work on the theory of electrolytic dissociation. We determined to make a comparatively thorough study of cane-sugar, using solutions much more concentrated than those employed by Arrhenius. We found that we could work to a concentration of twice normal. The freezing-point lowerings given in Table XXXVII. are plotted in Fig. III.

Cane-sugar shows very considerable hydration. The curve showing the complexity of the hydrates of cane-sugar is given in Fig. IV.

[1] Ztschr. phys. Chem., 2, 495 (1888).

Table XXXVII.—Freezing-point Measurements.

Cane-Sugar, $C_{12}H_{22}O_{11}$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.404	2.02
0.4	0.848	2.12
0.6	1.345	2.24
0.8	1.950	2.44
1.0	2.662	2.66
1.2	3.550	2.96
1.4	4.612	3.29
1.6	5.800	3.62
1.8	7.230	4.02
2.0	9.130	4.57

Table XXXVIII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_{12}H_{22}O_{11}}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.5904	1.7100	23.8804	4.48
0.4	26.2388	3.4200	22.8188	8.72
0.6	26.8635	5.1300	21.7335	13.06
0.8	27.5078	6.8400	20.6678	17.33
1.0	28.0680	8.5500	19.5180	21.93
1.2	28.6920	10.2600	18.4320	26.27
1.4	29.3441	11.9700	17.3741	30.50
1.6	29.8762	13.6800	16.1962	35.22
1.8	30.4824	15.3900	15.0924	39.63
2.0	31.1005	17.1000	14.0005	44.0

Table XXXIX.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.	M.	H.
0.2	1.86	2.02	1.93	2.0	10.0
0.4	1.86	2.12	1.94	2.3	5.8
0.6	1.86	2.24	1.95	2.5	4.2
0.8	1.86	2.44	2.02	4.4	5.5
1.0	1.86	2.66	2.07	5.5	5.5
1.2	1.86	2.96	2.18	8.1	6.7
1.4	1.86	3.29	2.29	10.4	7.4
1.6	1.86	3.62	2.35	11.6	7.2
1.8	1.86	4.02	2.43	13.0	7.2
2.0	1.86	4.57	2.56	15.2	7.6

Organic Acids.

The organic acids really belong in the class of the electro-

lytes. But since they are, generally speaking, weakly dissociated compounds, they have been studied as a class by themselves. Some of these substances contain a small amount of water of crystallization, but, generally, they crystallize either without water or with only a small amount.

Five organic acids have thus far been studied, and the results are given below. The symbols in the following tables have exactly the same significance as in the preceding. Organic acids being electrolytes, their conductivities were measured. These are recorded in the tables headed "conductivity measurements." v is the volume of the solutions, μ_v their molecular conductivities, and α their dissociation.

Acetic Acid.

Acetic acid being soluble in water in all proportions, we worked to ten-normal concentration. Although the observed freezing-point lowering increased with the concentration, the corrected lowering decreased regularly from the most dilute to the most concentrated solution studied.

The corrected lowering found experimentally was less than the theoretical lowering at all concentrations except the most dilute. This shows that acetic acid in water is polymerized, and that the amount of the polymerization is greater the more concentrated the solution. This is exactly in accord with what was pointed out a year ago by Jones and Murray[1] in their investigation on the effect of one associated liquid on the association of another associated liquid. They showed that water—an associated liquid—diminishes the association of acetic acid—also a strongly associated liquid—and that the magnitude of this effect is a function of the amount of water relative to the amount of acetic acid present. The more concentrated the solution of acetic acid the greater will be the complexity of its molecules. A few of the freezing-point data for acetic acid are plotted in Fig. V. The conductivities of acetic acid are perfectly normal and are plotted in Fig. VI.

Acetic acid shows no evidence of the formation of hydrates except, possibly, in the most dilute solution studied.

[1] This JOURNAL, 30, 193 (1903).

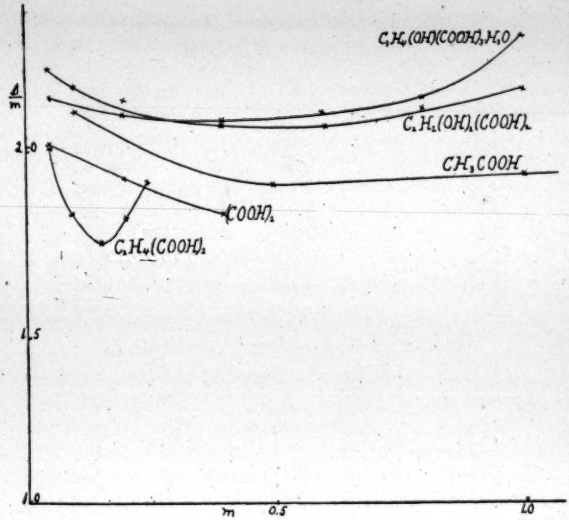
$C_4H_4(OH)(COOH)_2H_2O$
$C_4H_4(OH)_2(COOH)_2$
CH_3COOH
$(COOH)_2$
$C_4H_4(COOH)_2$
$\frac{\Delta}{m}$
2.0
1.5
1.0
0
m
0.5
1.0

Fig. V.

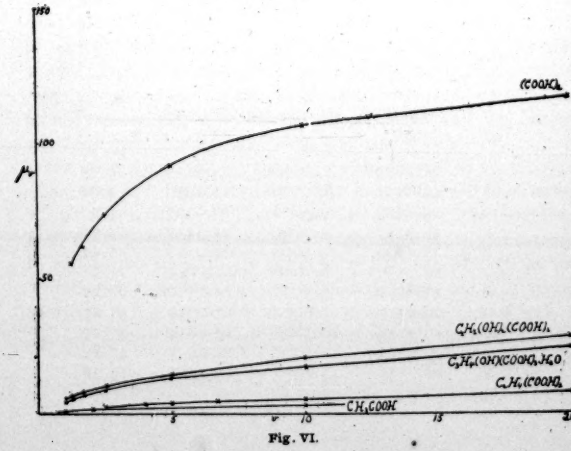
150
100
50
μ_v
$(COOH)_2$
$C_4H_4(OH)_2(COOH)_2$
$C_4H_4(OH)(COOH)_2H_2O$
$C_4H_4(COOH)_2$
CH_3COOH
5
v
10
15
20

Fig. VI.

Table XL.—Freezing-point Measurements.

Acetic acid, $CH_3.COOH$.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0.210	2.10
0.5	0.945	1.89
1.0	1.908	1.91
2.0	4.000	2.00
3.0	6.190	2.06
4.0	8.260	2.06
5.0	10.500	2.10
6.0	13.000	2.17
7.0	15.200	2.17
8.0	18.000	2.25
10.0	24.000	2.40

Table XLI.—Conductivity Measurements.

Acetic acid, $\mu_v = 2.73$.

v.	μ_v.	α.
0.1	0.04	
0.125	0.07	
0.14	0.10	
0.16	0.14	
0.20	0.19	
0.25	0.25	
0.33	0.35	0.1
0.5	0.52	0.2
1.0	0.85	0.3
2.0	1.33	0.5
10.0	3.07	1.1

Table XLII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.1	24.9635	0.1500	24.8135	0.75
0.5	25.0450	0.7500	24.2950	2.82
1.0	25.1337	1.5000	23.6337	5.47
2.0	25.3257	3.0000	22.3257	10.70
3.0	25.5228	4.5000	21.0228	15.91
4.0	25.7159	6.0000	19.7159	21.14
5.0	25.8570	7.5000	18.3570	26.57
6.0	26.0329	9.0000	17.0329	31.87
7.0	26.1834	10.5000	15.6834	37.27
8.0	26.2843	12.0000	14.2843	42.86
10.0	26.5551	15.0000	11.5551	53.78

Table XLIII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.
0.1	0.010	1.89	2.10	2.08
0.5	0.005	1.87	1.89	1.84
1.0	0.003	1.86	1.91	1.80
2.0	....	1.86	2.00	1.78
3.0	....	1.86	2.06	1.73
4.0	....	1.86	2.06	1.63
5.0	....	1.86	2.10	1.53
6.0	....	1.86	2.17	1.48
7.0	....	1.86	2.17	1.38
8.0	....	1.86	2.25	1.18
10.0	....	1.86	2.40	1.10

Oxalic Acid.

The freezing-point lowerings produced by oxalic acid decrease with increase in concentration, falling below the theoretical value if oxalic acid was not dissociated—Table XLIV. Oxalic acid is, however, very appreciably dissociated, as is shown in Table XLV.

When the corrected molecular lowering L′, Table XLVII., is compared with the molecular lowering L, calculated on the basis of the dissociation of the acid as given in Table XLV., it will be seen that the value found experimentally is much less than the calculated value, at all dilutions studied. This shows that oxalic acid, like acetic acid, undergoes polymerization in solution, and there is no evidence of the existence of hydrates in such solutions. The freezing-point and conductivity data for oxalic acid are given in Figs. V. and VI.

Table XLIV.—Freezing-point Measurements.

Oxalic acid, $(COOH)_2$.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.101	2.01
0.1	0.207	2.07
0.2	0.382	1.91
0.4	0.725	1.81

Table XLV.—Conductivity Measurements.

Oxalic acid, $\mu\infty^{\circ} = 295$.

v.	μ_v.	α.
1.25	55.4	18.0
1.67	61.66	22.0
2.5	73.75	25.0
5.0	91.44	31.0
10.0	106.5	36.0
20.0	117.8	39.0

Table XLVI.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	24.9785	0.1125	24.8660	0.54
0.1	25.0174	0.2250	24.7924	0.83
0.2	25.1012	0.4500	24.6512	1.40
0.4	25.2235	0.9000	24.3235	2.71

Table XLVII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.
0.05	0.39	3.31	2.01	2.00
0.1	0.36	3.18	2.07	2.05
0.2	0.31	3.01	1.91	1.88
0.4	0.25	2.79	1.81	1.75

Succinic Acid.

The freezing-point lowerings of succinic acid pass through a minimum (Table XLVIII.). The corrected lowerings of succinic acid also pass through a minimum (L′, Table LI.). If the corrected lowerings found experimentally be compared with the lowerings calculated from dissociation, the former will be seen to be always less than the latter. This would show that succinic acid, like oxalic acid, is somewhat polymerized in solution, but the polymerization is less than in the case of oxalic acid.

The freezing-point and conductivity data for succinic acid are plotted in curves, Figs. V. and VI.

Table XLVIII.—Freezing-point Measurements.

Succinic acid, $C_2H_4(COOH)_2$.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.100	2.00
0.1	0.180	1.80
0.15	0.260	1.73
0.2	0.360	1.80
0.25	0.475	1.90

Table XLIX.—Conductivity Measurements.

Succinic acid, $\mu\infty^\circ = 209$.

v.	μ_v.	α.
2.5	2.54	1.2
4.0	3.46	1.6
5.0	3.94	1.9
6.7	4.54	2.1
10.0	5.33	2.5
20.0	7.30	3.5

Table L.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	24.9731	0.1475	24.8256	0.70
0.10	25.0379	0.2950	24.7429	1.03
0.15	25.0625	0.4425	24.6200	1.44
0.20	25.0839	0.5900	24.4939	2.02
0.25	25.1448	0.7375	24.4073	2.37
0.40	25.2518	1.1800	24.0718	3.71

Table LI.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.
0.05	0.035	1.99	2.00	1.99
0.10	0.025	1.95	1.80	1.78
0.15	0.021	1.94	1.73	1.71
0.20	0.019	1.93	1.80	1.74
0.25	0.016	1.92	1.90	1.83

Tartaric Acid.

There is a well-defined minimum in the molecular lowerings, $\frac{\Delta}{m}$, of tartaric acid. This is seen in Table LII., and in Fig. V. The minimum also appears in column L′, Table

LV., which is the molecular lowerings corrected for specific gravities.

The corrected molecular lowerings for tartaric acid are very nearly identical with the molecular lowerings calculated from the dissociation, L, Table LV. This is true for all of the dilutions studied. Tartaric acid is, then, an example of a compound which undergoes neither polymerization nor hydration in solution.

The conductivities of tartaric acid are perfectly normal, as shown by the curve in Fig. VI.

Table LII.—Freezing-point Measurements.

Tartaric acid, $C_2H_2(OH)_2(COOH)_2$.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.111	2.22
0.1	0.217	2.17
0.2	0.425	2.13
0.4	0.826	2.06
0.6	1.230	2.05
0.8	1.680	2.10
1.0	2.150	2.15

Table LIII.—Conductivity Measurements.

Tartaric acid, $\mu\infty^\circ = 300$.

v.	μ_v.	α.
1.0	5.76	1.9
1.25	6.69	2.2
1.67	8.02	2.7
2.5	10.13	3.4
5.0	14.34	4.8
10.0	20.54	6.5
20.0	28.05	9.5

Table LIV.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.0124	0.1875	24.8249	0.70
0.1	25.0973	0.3750	24.7223	1.11
0.2	25.2584	0.7500	24.5084	1.97
0.4	25.5930	1.5000	24.0930	3.63
0.6	25.9172	2.2500	23.6672	5.33
0.8	26.3938	3.0000	23.3938	6.42
1.0	26.5651	3.7500	22.8151	8.74

Table LV.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L'.
0.05	0.094	2.22	2.22	2.20
0.1	0.065	2.10	2.17	2.15
0.2	0.048	2.04	2.13	2.09
0.4	0.034	1.99	2.06	1.99
0.6	0.027	1.96	2.05	1.94
0.8	0.022	1.94	2.10	1.97
1.0	0.019	1.93	2.15	1.96

Citric Acid.

Column $\frac{\Delta}{m}$, Table LVI., shows a well-defined minimum in the molecular freezing-point lowerings of citric acid. This is seen in the citric acid curve, Fig. V., and in the corrected molecular lowerings for citric acid, L', Table LIX. Citric acid is another example of a compound that shows neither polymerization nor hydration in solution. The corrected experimental values in column L' agree closely with the values calculated from the dissociation of the acid, as given in column L, Table LIX.

The conductivity curve of citric acid is of the same nature and magnitude as that of the other organic acids which we studied with the exception of oxalic acid, which has a much larger conductivity.

Table LVI.—Freezing-point Measurements.

Citric acid, $C_3H_4(OH)(COOH)_3.H_2O$.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.107	2.14
0.1	0.207	2.07
0.2	0 418	2.09
0.4	0.830	2.07
0.6	1.253	2.09
0.8	1.707	2.13
1.0	2.230	2.30

Table LVII.—Conductivity Measurements.

Citric acid, $\mu\infty^{\circ} = 630$.

v.	μ_v.	α.
1.0	4.23	0.7
1.25	5.33	0.8
1.67	6.99	1.1
2.5	7.49	1.3
5.0	13.04	2.0
10.0	17.6	2.8
20.0	24.2	3.8

Table LVIII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	24.8406	0.2625	24.5781	1.69
0.1	25.1212	0.5250	24.5962	1.61
0.2	25.2869	1.0500	24.2369	3.05
0.4	25.8255	2.1000	23.7255	5.10
0.6	26.0707	3.1500	22.9207	8.32
0.8	26.4768	4.2000	22.2768	9.89
1.0	26.8365	5.2500	21.5865	13.65

Table LIX.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L'.
0.05	0.038	2.07	2.14	2.10
0.1	0.020	2.02	2.07	2.04
0.2	0.020	1.97	2.09	2.03
0.4	0.013	1.93	2.07	1.97
0.6	0.011	1.92	2.09	1.92
0.8	0.008	1.90	2.13	1.92
1.0	0.007	1.89	2.30	1.99

General Conclusions.

1. Of the thirteen non-electrolytes studied in this investigation only glycerol showed any marked hydration or power to combine with the solvent. Glycerol combines with water to about the same extent as the ternary or even some of the quaternary electrolytes.

2. Cane-sugar and fructose also show considerable power to combine with water, but this is not even of the same order of magnitude as that shown by glycerine.

3. Methyl and ethyl alcohol also show some slight power to combine with water in solution.

4. A number of the non-electrolytes studied show a marked tendency to undergo polymerization in the presence of water.

5. The fact that certain non-electrolytes combine with water, forming hydrates, shows that molecules as well as ions can form hydrates, and leaves it an open question as to whether it is the molecules or the ions that combine with water in the case of the electrolytes.

6. None of the organic acids studied in this investigation show any appreciable tendency to combine with water in solution.

7. Some of the organic acids show a marked tendency to undergo polymerization in aqueous solution.

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May, 1904.

THE EXISTENCE OF ALCOHOLATES IN SOLUTIONS OF CERTAIN ELECTROLYTES IN ALCOHOL.

BY HARRY C. JONES AND FREDERICK H. GETMAN (CARNEGIE RESEARCH ASSISTANT).

Having found that such a large number of electrolytes[1] and and some non-electrolytes[2] combine with water in aqueous solution, we naturally turned our attention to solutions in solvents other than water. A careful study of some work that we had already done[3] in ethyl alcohol as the solvent, using the boiling-point method, would indicate that certain electrolytes combine with alcohol when in solution in that solvent. An examination of the curves[4] will show that the molecular rise produced by the five electrolytes there studied —sodium bromide, cadmium iodide, potassium iodide, ammonium iodide, and sodium iodide—is greater at some dilution than the theoretical molecular rise in ethyl alcohol. Like the large values found for freezing-point lowering, this indicates

[1] Ztschr. phys. Chem., 46, 244; Phys. Rev., 18, 146; This JOURNAL, 31, 303.
[2] This JOURNAL, 32, 308.
[3] *Ibid.*, 31, 338.
[4] *Ibid.*, 31, 342.

that a part of the solvent is combined with the dissolved substance.

To test this matter still further, other electrolytes have been employed and the molecular rise produced by them carefully measured, using the Jones boiling-point apparatus.[1] The results of these measurements are given below: m is the concentration in terms of gram-molecules of salt in 1,000 grams of solvent, ρ the observed rise in boiling-point, and $\frac{\rho}{m}$ the molecular rise in the boiling-point.

Table I.—LiCl in Ethyl Alcohol. First Series.

m.	ρ.	$\frac{\rho}{m}$.
0.07	0.09	1.28
0.22	0.30	1.37
0.28	0.40	1.43
0.39	0.565	1.45
0.64	0.98	1.53
0.77	1.23	1.58
0.815	1.30	1.59
1.92	1.53	1.66
1.09	1.885	1.73
1.28	2.410	1.89
1.51	3.03	2.00
1.63	3.435	2.10
1.77	3.79	2.14
2.07	5.03	2.43

Table II.—LiCl in Ethyl Alcohol. Second Series.

m.	ρ.	$\frac{\rho}{m}$.
0.07	0.09	1.28
0.19	0.255	1.34
0.31	0.44	1.42
0.44	0.65	1.48
0.59	0.91	1.54
0.73	1.145	1.57
0.94	1.59	1.69
1.15	2.10	1.82
1.46	2.95	2.02
1.62	3.42	2.11

[1] This JOURNAL, 19, 581.

Table III.—$LiNO_3$ in Ethyl Alcohol. First Series.

m.	ρ.	$\frac{\rho}{m}$.
0.08	0.11	1.38
0.13	0.17	1.30
0.19	0.25	1.31
0.35	0.47	1.34
0.39	0.54	1.38
0.51	0.71	1.39
0.84	1.21	1.44
1.21	1.87	1.54
1.46	2.34	1.60

Table IV.—$LiNO_3$ in Ethyl Alcohol. Second Series.

m.	ρ.	$\frac{\rho}{m}$.
0.06	0.085	1.42
0.09	0.120	1.33
0.18	0.234	1.30
0.27	0.355	1.31
0.38	0.515	1.36
0.48	0.655	1.36
0.58	0.810	1.40
0.71	1.010	1.42
0.95	1.415	1.48
1.27	2.010	1.58
1.46	2.385	1.63
1.67	2.770	1.65

Table V.—$Ca(NO_3)_2$ in Ethyl Alcohol. First Series.

m.	ρ.	$\frac{\rho}{m}$.
0.03	0.04	1.33
0.08	0.10	1.25
0.14	0.17	1.21
0.19	0.22	1.16
0.26	0.295	1.13
0.37	0.42	1.13
0.47	0.515	1.09
0.57	0.62	1.08
0.74	0.81	1.09
0.83	0.91	1.09

Table VI.—$Ca(NO_3)_2$ in Ethyl Alcohol. Second Series.

m.	ρ.	$\frac{\rho}{m}$.
0.06	0.08	1.33
0.14	0.17	1.21
0.21	0.21	1.16
0.30	0.34	1.13
0.37	0.40	1.09
0.45	0.50	1.11
0.66	0.71	1.08

The molecular rise in the boiling-point of ethyl alcohol produced by lithium chloride and nitrate is greater at practically all the concentrations studied than would be calculated from

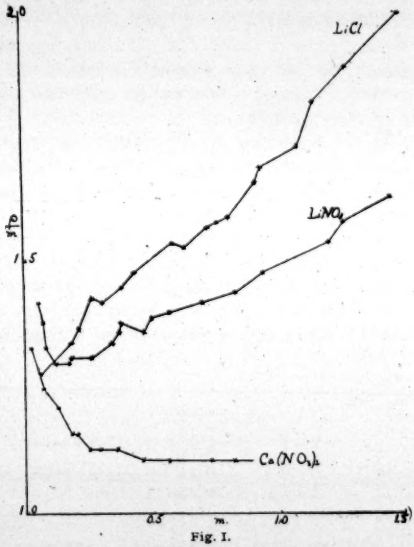


Fig. I.

its dissociation. Calcium nitrate fulfils this same condition in dilute solutions, but not in concentrated.

The results recorded in Tables I. to VI. are plotted as curves, Fig. I. The abscissa represents concentration and the ordinate molecular rise in boiling-point. The curves for the two salts of lithium rise rapidly with increasing concentration, being at practically all concentrations above the calculated curve.

The curve for calcium nitrate in the more dilute solutions rises above the theoretical curve, but rapidly drops to a value agreeing closely with it.

We interpret these results in ethyl alcohol, obtained by the boiling-point method, in the same way that we interpreted the abnormal freezing-point lowerings in water.

The dissolved substance probably combines with a portion of the alcohol, removing it from the field of action as far as rise in boiling-point is concerned. There being, therefore, less alcohol present acting as solvent, the rise in the boiling-point is greater than we would expect from the amount of dissolved substance present.

As far as the formation of alcoholates in solution is concerned, this is, of course, purely qualitative. We hope, however, in the near future, to be able to obtain the data necessary to calculate quantitatively the approximate composition of the alcoholates in such solutions, just as we have already calculated the composition of the hydrates in aqueous solutions of a large number of electrolytes and a few non-electrolytes.

A further study of aqueous solutions, together with solutions in the alcohols and other solvents, will be made as rapidly as possible.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
May, 1904.

Contributions from the Sheffield Laboratory of Yale University.

CXIX.—RESEARCHES ON PYRIMIDINES: 2-OXY-4,6-DIAMINOPYRIMIDINE.[1]

[SEVENTH PAPER.]

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

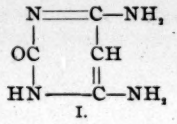
In this paper we describe a number of pyrimidines derived from 2-thiobarbituric acid. Our chief object in investigating

[1] Part of a thesis presented by Mr. G. S. Jamieson for the degree of Doctor of Philosophy, Yale University, 1904.

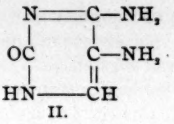
these compounds was to prepare 2-oxy-4,6-diaminopyrimidine.

Kutscher[1] believes he obtained an oxydiaminopyrimidine from yeast nucleic acid, the acid having been decomposed by sulphuric acid at a high temperature and under pressure. He considers the substance as differing from cytosine inasmuch as a hydrogen atom is replaced by an amino group.

It may be added that since the pyrimidine derivatives hitherto obtained from nucleic acids have an oxygen atom in the 2-position, for example, uracil, thymine, and cytosine, it is probable that a diamino derivative would be similarly constituted. This being the case, there are only two oxydiaminopyrimidines that fulfil these conditions, namely, 2-oxy-4,6-diaminopyrimidine (I.) and 2-oxy-5,6-diaminopyrimidine (II.):

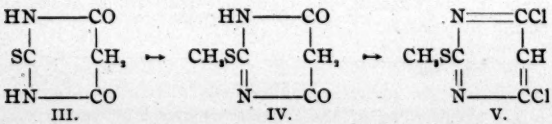


I.



II.

Our first attempts to prepare the oxydiaminopyrimidine represented by Formula I. were as follows: 2-Thiobarbituric acid (III.) was prepared by the method of Michael.[2] It was found that this substance could be converted into 2-methylmercapto-4,6-dioxypyrimidine (IV.) by means of sodium ethylate and methyl iodide in alcoholic solution:



III. IV. V.

When the mercapto derivative (IV.) was heated on the steam-bath with 2 molecular proportions of phosphorus pentachloride, it was converted into 2-methylmercapto-4,6-dichlorpyrimidine (V.). The reaction was not smooth and a con-

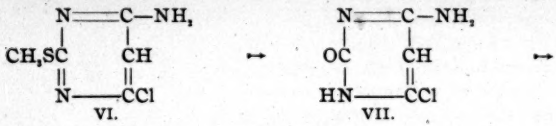
[1] Ztschr. physiol. Chem., **38**, 176 (1903).

[2] J. prakt. Chem., **35**, 456 (1887); **49**, 38 (1894).

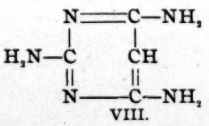
siderable amount of decomposition-products was always obtained. It was later observed that the dichloride could be obtained more smoothly by using phosphorus oxychloride instead of the pentachloride.

When the dichloride was heated with alcoholic ammonia it was found that only one chlorine atom was easily removed and 2-mercapto-5-chlorcytosine (VI.) was formed. This took place at temperatures ranging from 125° to about 190°. Even below the latter temperature mercaptan was evolved, and above 190° 2,4,6-triaminopyrimidine (VIII.), which has been described by Gabriel,[1] was obtained. There seemed to be little tendency for the two chlorine atoms to react without also displacing the mercapto group.

The 2-mercapto-4-chlorcytosine was then converted into 4-chlorcytosine (VII.) by boiling with hydrochloric acid. When this was heated with alcoholic ammonia a reaction took place, but the chief product was not the desired 2-oxy-4,6-aminopyrimidine:



VI. VII.

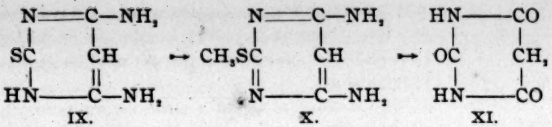


VIII.

It was finally found that 2-oxy-4,6-diaminopyrimidine could easily be prepared from 2-thio-4,6-diaminopyrimidine (IX.) which Traube[2] has recently obtained by condensing malonic nitrile with thiourea. This substance united smoothly with methyl iodide and the resulting mercapto derivative (X.) formed on treating the addition-product with ammonia, on carefully boiling with hydrochloric acid, gave the 2-oxy-4,6-diaminopyrimidine (I.):

[1] Ber. d. chem. Ges., 34, 3364.

[2] Ann. Chem. (Liebig), 331, 80 (1904).

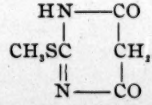


IX. X. XI.

It was then found that if the warming with hydrochloric acid was continued for more than a short time on the steam-bath the 2-oxy-4,6-diaminopyrimidine was completely converted into barbituric acid (XI.). It is therefore obvious, from the readiness with which this compound is decomposed by hydrochloric acid, that it is not identical with Kutscher's new base. If the latter is an oxydiaminopyrimidine it probably is 2-oxy-5,6-diaminopyrimidine.

EXPERIMENTAL PART.

2-Thiobarbituric acid was prepared according to Michael's[1] directions, by the condensation of sodium ethyl malonate with thiourea in absolute alcoholic solution. Twenty-five grams of ethyl malonate gave 20 grams of crude sodium thiobarbiturate. From this a yield of 12 grams of acid was obtained. It was found that if instead of the calculated quantity of sodium ethylate two molecular proportions were used a larger yield of the acid resulted. For example, in two experiments, using 25 grams of ethyl malonate, 27 grams of sodium thiobarbiturate were obtained; in three other cases, using the same proportions, 28 grams of salt separated, the yield of thiobarbituric acid in each case being 16.5 grams.

2-Methylmercaptobarbituric Acid,  .—The best yield of this substance was obtained when 12 grams of thiobarbituric acid were added to a cold, absolute alcoholic solution of 1.9 grams of sodium, then 15 grams of methyl iodide were added and the solution was not allowed to warm. The reaction was complete in two days. The alcohol and

[1] J. prakt. Chem., **35**, 456 (1887); **49**, 38 (1894).

excess of methyl iodide were then evaporated and the residue was treated with water and acidified with acetic acid. The precipitate was filtered, washed with water, absolute alcohol, and ether. A yield of 8.6 grams of sodium-free material was obtained. In another experiment, 40 grams of acid gave 2.5 grams of the mercapto derivative, the usual yield being between 53 and 66 per cent of the calculated. Attempts to methylate thiobarbituric acid by other methods, such as by direct addition of methyl iodide, or by the action in alcoholic ammonia, or in aqueous solution and in the presence of alkali, either failed entirely or did not give as satisfactory results as the above method.

The 2-methylmercaptobarbituric acid crystallized from water in needles. It is sparingly soluble in hot water and less soluble in alcohol. It did not melt at 300°, but gradually turned a light-brown. A nitrogen determination gave :

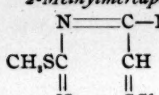
	Calculated for $C_5H_4O_2N_2S$.	Found.
N	17.72	17.87

2-Methylmercapto-4,6-dichlorpyrimidine, $CH_3SC(N{=}CCl{-}CH{=}N{-}CCl)$. — Four grams of the above 2-methylmercaptobarbituric acid were heated with 9 grams of phosphorus pentachloride on the steam-bath. When the evolution of hydrogen chloride ceased the dark-red solution was cooled and treated with crushed ice. The dichloride was then shaken out with ether, the ethereal solution dried over calcium chloride, evaporated, and the residue distilled at 28 mm. pressure, whereupon 2.5 grams of colorless oil were obtained, boiling at 154°, this being a yield of 50.2 per cent of the calculated. In two other experiments with phosphorus pentachloride, using in each case 8 grams of the methylmercaptobarbituric acid, 3 grams and 3.7 grams of dichloride were obtained. Both specimens boiled at 135° to 136° at 14 mm. pressure. The oil thus obtained solidified in the form of table-like prisms, which melted at 41° to 42°. When phosphorus oxychloride was used instead

of the pentachloride, the remaining treatment being the same, the dichloride was directly obtained in the crystalline condition, it being unnecessary to distil under reduced pressure. The material from the ethereal solution was purified by recrystallizing from a little alcohol. It then formed stout, pointed prisms and the melting-point was not altered. It is very soluble in ether, alcohol, and petroleum ether. In two experiments, using 5 grams of the methylmercaptobarbituric acid, 3.3 grams and 3.4 grams of the dichloride were obtained. The yield by the action of either the pentachloride or the oxychloride of phosphorus, especially in large quantities, was found to be very irregular. A nitrogen determination gave:

	Calculated for $C_5H_4N_2SCl_2$.	Found.
N	14.36	14.76

2-Methylmercapto-4-chlor-6-aminopyrimidine,



.—Two and a half grams of the 2-methylmercapto-4,6-dichlorpyrimidine were heated in a sealed tube with about 75 cc. of alcoholic ammonia for four hours at 125° to 126°. On cooling, the ammonium chloride which had separated was filtered and the filtrate evaporated. The residue was purified by recrystallizing from water, in which it was difficultly soluble. It crystallized in colorless, needle-like prisms, which melted at 127° to 128° to a colorless liquid. A yield of 1.5 grams of purified material was obtained. Four other experiments gave the following yields:

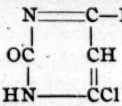
Chloride. Grams.	Monoamine. Grams.
3.7	2.6
3.0	2.2
3.2	2.7
3.3	2.6

A nitrogen determination gave:

	Calculated for $C_5H_6N_3SCl$.	Found.
N	23.93	24.04

Action of Alcoholic Ammonia.—This chloraminopyrimidine (1.1 grams) was heated with about 75 cc. of alcoholic ammonia (alcohol saturated with dry ammonia at 0°) at 145° for three hours and then for two hours at 150°, whereupon the material was recovered completely unaltered. The 1.1 grams of substance were reheated with the same volume of fresh alcoholic ammonia at 170° for two hours, and then at 190° for a half hour; 0.7 gram of unaltered material was obtained.

Two and four-tenths grams of the chloraminopyrimidine were heated with alcoholic ammonia for two hours at 185° to 190°, and four hours at 215° to 220°. On opening the tube the alcohol was found to be saturated with mercaptan. A considerable amount of a light-yellow precipitate had separated from the alcohol. This was filtered, washed with alcohol and then with water. It melted at about 234° to 240° and it gave an alkaline reaction to turmeric paper. It contained neither sulphur nor chlorine and was found to be 2,4,6-triaminopyrimidine, which has been described by Gabriel.[1]

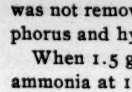
4-Chlorcytosine,  .—This was obtained by boiling 0.5 gram of the above mercapto derivative with concentrated hydrochloric acid. Mercaptan was readily evolved and upon evaporating the solution, 4-chlorcytosine hydrochloride was obtained. This crystallized from hot water in balls of very small, slender, hard prisms or needles. From dilute aqueous solutions of this salt, ammonia precipitates a crop of flat, colorless prisms; from more concentrated solutions the base separates as a jelly resembling thick starch paste, which is difficult to filter. When dried on paper it adheres strongly to the fiber. It is fairly soluble in water and it does not melt at 300°, although it sinters and gradually turns red. A nitrogen determination gave:

	Calculated for $C_4H_4ON_3Cl$.	Found.
N	28.86	28.73

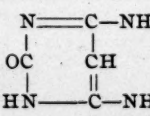
[1] Ber. d. chem. Ges., 34, 3364.

The chlorine in this compound is very firmly bound. It was not removed by tin and hydrochloric acid, or by red phosphorus and hydriodic acid.

When 1.5 grams of this material were heated with alcoholic ammonia at 183° for two hours 0.95 gram of substance insoluble in alcoholic ammonia was formed. It was difficultly soluble in water; if the solution was cooled rapidly, very small crystals were obtained; if slowly cooled, little balls were formed. This substance did not melt at 307°. It was free from chlorine and a nitrogen determination gave only 24.9 per cent nitrogen. It was not identified, since two attempts to prepare the compound failed on account of the explosion of the sealed tubes and no time was available to repeat the work.

2-Methylmercapto-4,6-diaminopyrimidine,  .—Malonic nitrile and thiourea were condensed according to Traube's[1] directions in an alcoholic solution with sodium ethylate. Two grams of the 2-thio-4,6-diaminopyrimidine were moistened with alcohol and 2.2 grams of methyl iodide were added. The mixture stood two hours without change. Suddenly, heat was evolved and the solution solidified. The alcohol was evaporated and the residue was dissolved in water. Ammonia then precipitated 2.2 grams of colorless crystalline material. This was quite soluble in hot water, from which, on cooling, it separated in the form of slender prisms. It melted at 185° to 186° with a little effervescence, and a nitrogen determination gave:

	Calculated for $C_5H_8N_4S$.	Found.
N	35.89	35.94

2-Oxy-4,6-diaminopyrimidine,  .—One gram

[1] Ann. Chem. (Liebig), 331, 80 (1904).

of the 2-methylmercapto-4,6-diaminopyrimidine was evaporated twice with about 20 cc. of concentrated hydrochloric acid on the steam-bath. Methylmercaptan was evolved and the residue crystallized from water. The monohydrochloride which separated formed long, slender prisms which did not melt at 307°. This salt was dissolved in water and an excess of ammonium hydroxide was added, whereupon a fine crystalline meal was precipitated. It was difficultly soluble in hot water, and it separated as slender, rectangular, anhydrous prisms. When the material was heated it became gradually yellow at about 297° and remained a dry, yellow powder at 347°. A nitrogen determination gave :

	Calculated for $C_4H_6ON_4$.	Found.
N	44.44	44.82

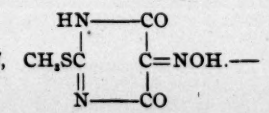
The *picrate* separated from hot water when slowly cooled in the form of thin tables. If rapidly cooled it formed bunches of slender prisms. It had a bright yellow color, and a nitrogen determination showed that it was a monopicrate :

	Calculated for $C_{10}H_9O_8N_7$.	Found.
N	27.60	27.46

It sinters at about 185° and melts with effervescence at 210° to 214°.

It was found that if the 2-methylmercapto-4,6-diaminopyrimidine was warmed with hydrochloric acid for a longer time than was sufficient to expel the mercaptan, barbituric acid was obtained. This was identified by its crystallizing with water of crystallization and by the following nitrogen determination in the dried material :

	Calculated for $C_4H_4O_3N_2$.	Found.
N	21.89	22.36

2-Methylmercaptovioluric Acid, 

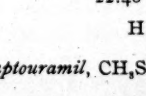
Eight grams of 2-methylmercapto-4,6-dioxypyrimidine were

dissolved in 150 cc. of water containing 2 grams of sodium hydroxide. Four grams of sodium nitrite were added and the solution was acidified with acetic acid. The solution turned dark-blue when acidified, but gradually became red. A brick-red precipitate formed after the solution stood ten hours and 4.55 grams of the isonitrosopyrimidine were obtained, or 48 per cent of the calculated. It became dark-colored when heated and gradually decomposed at 180° to 200°. The ammonium and sodium salts have a purple color. Some of the sodium salt was dissolved in warm water and acidified with hydrochloric acid. The solution became red, and, on standing, it deposited red, flat, pointed prisms, which contained 2 molecules of water of crystallization. The water was determined by heating the material at 120°.

	Calculated for $C_5H_6O_3N_3S.2H_2O$.	Found.
H_2O	11.66	11.84

A nitrogen determination in the case of the anhydrous material gave :

	Calculated for $C_5H_6O_3N_3S$.	Found.
N	22.46	22.22

2-Methylmercaptouramil,  . — This was obtained from the above isonitrosopyrimidine by reduction with ammonium sulphide according to Traube's method.[1] This material is difficultly soluble in water or hydrochloric acid, dilute or concentrated. It is soluble in sodium hydroxide and it is precipitated by acetic acid, in which it is difficultly soluble. A nitrogen determination gave :

	Calculated for $C_5H_7O_2N_3S$.	Found.
N	24.28	24.37

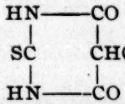
Attempts to chlorinate this material by means of phosphorus oxychloride did not lead to a smooth result. The

[1] Ann. Chem. (Liebig), **331**, 82 (1904).

material turns brown on heating at 285° but does not melt at 301°.

The following pyrimidine derivatives were prepared by Dr. Henry F. Merriam in the course of some work on isomers of histidine. The work was interrupted by the departure of Mr. Merriam from this laboratory.

2-Thio-5-methylbarbituric Acid,



—Seven and eight-tenths grams of sodium were dissolved in alcohol and the solution added to 60 grams of methylmalonic ethyl ester. A hot alcoholic solution of 26 grams of thiourea was then added and the mixture heated gently on the steam-bath for five hours. The white sodium salt was then filtered, dissolved in a small volume of hot water, and the solution acidified strongly with hydrochloric acid. On cooling, a mass of thin plates separated. After crystallizing from water the substance melted with effervescence at about 244.° The yield was 27 grams. 2-Thio-5-methylbarbituric acid crystallizes with 1 molecule of water of crystallization, which is evolved at 120°.

	Calculated for $C_5H_6O_2N_2S.H_2O$.	Found.
H_2O	18.55	18.25

A nitrogen determination in the case of the dried material gave:

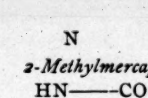
	Calculated for $C_5H_6O_2N_2S$.	Found.
N	17.72	18.04

2-Thio-5-ethylbarbituric Acid.—An alcoholic solution of 11 grams of sodium was added to 90 grams of ethylmalonic ethyl ester and a solution of 37 grams of thiourea in hot alcohol was added to the mixture, which was then warmed on the steam-bath for several hours. The white sodium salt was then removed by filtering and the free acid was liberated by means of hydrochloric acid. It separated from water in the form of long, needle-like prisms and it melted at 190° to 191°. It is

soluble in alcohol. The yield was 37 grams. It contains water of crystallization, which is given off at 120°. A nitrogen determination in the dry material gave :

	Calculated for $C_6H_8O_2N_2S$.	Found.
N	16.27	16.53

2-Methylmercapto-4,6-dioxy-5-methylpyrimidine,



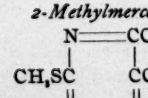
.—This compound was prepared by boiling 2-thio-5-methylbarbituric acid with alcohol and an excess of methyl iodide. After several hours the solid material was filtered and washed with alcohol. The material was almost insoluble in water and alcohol and it was purified by crystallizing from strong acetic acid. It formed short prisms which, on heating, decomposed with effervescence at about 303°. From 28 grams of thiomethylbarbituric acid 18.5 grams of the mercapto compound were obtained.

	Calculated for $C_6H_8O_2N_2S$.	Found.
N	16.27	16.23

2-Methylmercapto-4,6-dioxy-5-ethylpyrimidine.— Thirty-six grams of 5-ethylthiobarbituric acid, treated in the same manner as the above, except that in this case, after the action was complete, most of the alcohol was evaporated and the residue was treated with water, gave 25 grams of the mercapto compound. After crystallizing from acetic acid it melted with effervescence at about 257°. It was easily soluble in alcohol and acetic acid and difficultly soluble in water. A nitrogen determination gave :

	Calculated for $C_7H_{10}O_2N_2S$.	Found.
N	15.05	15.19

2-Methylmercapto-4,6-dichlor-5-methylpyrimidine,



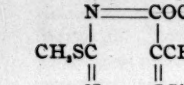
.—Ten and three-tenths grams of 2-methyl-

mercapto-4,6-dioxy-5-methylpyrimidine were heated on the steam-bath with 12.7 grams of phosphorus pentachloride. The material melted and, finally, the phosphorus oxychloride was removed by distilling in a vacuum. The residue was treated with ice-water and ether and the ethereal solution was dehydrated and distilled at 18 mm. pressure. The dichloride then boiled at 153° to 154°, and, on cooling, it crystallized in the form of colorless, stout prisms melting at 64°. The yield was 10.3 grams and a nitrogen determination gave:

	Calculated for $C_5H_4N_2SCl_2$.	Found.
N	13.39	13.48

As in the case of 2-methylmercapto-4,6-dichlorpyrimidine, only one chlorine atom is especially reactive in this compound.

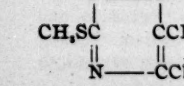
2-Methylmercapto-4-chlor-5-methyl-6-ethoxypyrimidine,



.—Seven grams of the above dichloride were dissolved in alcohol and 0.9 gram of sodium in alcoholic solution was added. The mixture was warmed for an hour on the steam-bath. The material was then precipitated with water and crystallized from alcohol, whereupon beautiful, colorless prisms were obtained melting at 85°. This substance is readily soluble in alcohol and benzene and insoluble in water. The yield was 6 grams. A nitrogen determination gave:

	Calculated for $C_9H_{11}ON_2SCl$.	Found.
N	12.81	13.18

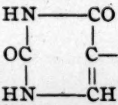
2-Methylmercapto-4-chlor-5-methyl-6-methylaminopyrimidine,



.—Nine grams of the above dichlor compound were heated at 145°, for three hours, with 5 grams

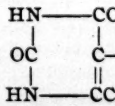
of methylamine in 58 cc. of alcohol. The solution was then evaporated, the residue washed with water and crystallized several times from alcohol. It formed stout prisms, which melted at 157°. The reaction was not complete and the yield was 5 grams. A nitrogen determination gave:

	Calculated for $C_7H_{10}N_2ClS$.	Found.
N	20.64	20.96



5-Dimethylaminouracil, OC C—N(CH$_3$)$_2$. — This compound, isomeric with histidine, was prepared by heating 5-bromuracil[1] with an excess of dimethylamine at 150° for six hours. The contents of the tube were evaporated, taken up in water, and boiled with animal charcoal. The material was then crystallized from water, in which it is moderately soluble when hot, and very difficultly soluble when cold. It formed small, thin, colorless plates or films, which melted with strong effervescence at about 297°. A nitrogen determination gave:

	Calculated for $C_6H_9O_2N_3$.	Found.
N	27.09	27.23



4-Methyl-5-methylaminouracil, OC C—NHCH$_3$. — Fifteen grams of 4-methyl-5-bromuracil, prepared according to the directions of Behrend,[2] were heated for six hours at 150° with an excess of aqueous methylamine. The contents of the tube were then heated on the steam-bath until the free methylamine was removed. The bromine was removed by means of silver sulphate, the excess of silver by hydrogen sulphide, and the sulphuric acid by barium hydroxide, and the excess of the latter was precipitated by carbon dioxide. Then, on concentrating the solution to a small volume, a

[1] Wheeler and Merriam: This JOURNAL, 29, 486 (1903).
[2] Ann. Chem. (Liebig), 231, 249.

beautiful crop of colorless prisms separated. After crystallizing from water containing a little alcohol the compound melted at 214°. When crystallized from water, in which it is very soluble, it contains 1 molecule of water of crystallization. The presence of much alcohol in the water causes the compound to crystallize in an anhydrous condition. Water was determined by heating the material at 120°.

	Calculated for $C_6H_9O_2N_3.H_2O$.	Found.
H_2O	10.40	10.26

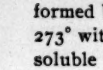
A nitrogen determination in the case of the dried material gave:

	Calculated for $C_6H_9O_2N_3$.	Found.
N	27.09	27.25

The *monohydrochloride* was prepared by dissolving the base in dilute hydrochloric acid and evaporating the solution. It formed beautiful, transparent, stout prisms, which melted at 273° with strong effervescence. The hydrochloride was less soluble in water than the free base, and the following analysis showed that the salt was anhydrous:

	Calculated for $C_6H_9O_2N_3.HCl$.	Found.
N	21.93	22.27

2-Methylmercapto-4,6-dimethylpyrimidine,



.—(By G. S. Jamieson.) Thirty-five grams of the methyl iodide addition-product of thiourea were dissolved in 30 cc. of water containing 9 grams of potassium hydroxide and 16 grams of acetylacetone were then added. The latter dissolved when the solution was shaken vigorously for a few seconds. The clear solution gradually became turbid, and, after standing for two days, a dark-yellow oil separated. This was shaken out with ether and the ethereal solution was dehydrated over potassium hydroxide. The oil was then distilled at 28 to 29 mm. pressure, whereupon it boiled

at 135° to 137°, leaving a notable residue. Six grams of colorless, odorless oil were obtained, a yield of 24.4 per cent of the calculated. Another condensation was made with three times the above quantities and 17.7 grams of oil were obtained which boiled at 144° at 33 mm. pressure and at 123° to 125° at 14 mm. pressure. The yield in this case was 23.9 per cent of the calculated. When the oil was cooled it solidified to a white, ice-like mass and melted at about 23° to 24°. The material is moderately soluble in cold water, and when the solution is warmed the substance separates in the form of oil drops, which dissolve again on cooling. It appears to absorb moisture from the air, since only by drying over sulphuric acid could agreeing results be obtained on analysis. Nitrogen determinations then gave:

	Calculated for $C_7H_{10}N_2S$.	Found. I.	II.
N	18.18	18.22	18.32

The residue, obtained as a by-product in this preparation, was not distilled, but when crystallized from alcohol, in which it was very soluble, it separated in the form of colorless, rectangular prisms, which melted at 153° to 154° to a clear liquid. A nitrogen determination agreed with the calculated for a dicyandiamide addition-product of 2-methylmercapto-4,6-dimethylpyrimidine or an isomer. It was not further examined.

2-Oxy-4,6-dimethylpyrimidine.—The above mercapto derivative, melting at 23° to 24°, was boiled with hydrobromic acid for three hours, evaporated, taken up in water, and neutralized with alkali. It was again evaporated and the dried, powdered material was extracted with benzene containing alcohol. The extracted material was crystallized twice from water, in which it was easily soluble. It melted at 198° to 199°. Evans[1] gives the melting-point of this substance, which he prepared by a different method, at 190° to 195°. Our material was shown to be identical with that of Evans by preparing the bromine derivative melting at 145° and by its behavior with diazobenzene chloride.

NEW HAVEN, CONN., June, 1904.

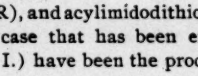
[1] J. prakt. Chem., **48**, 489 (1893).

Contributions from the Sheffield Laboratory of Yale University.

CXX.—ON THE ACTION OF PHENYLHYDRAZINE ON BENZOYLPSEUDOUREAS: 1,5-DIPHENYL-3-AMINOPYRRO-α,β'-DIAZOLE DERIVATIVES.

By Treat B. Johnson and George A. Menge.

Several papers[1] have appeared from this laboratory describing the behavior of phenylhydrazine towards acylthiocarbamates, RCO.NHCSOR, RCONHCOSR, acyldithiocarbamates, RCONHCSSR, acylimidothiocarbonates, RCON=C(OR)(SR), and acylimidodithiocarbonates, RCON=C(SR)$_2$. In every case that has been examined 1,5-dialkyltriazoles (Formula I.) have been the products of the reaction:



I.

One would be led to believe from these results that the relative tendency of the groups—CSalk., CS, CO, COalk.—to react with the hydrogen of the amino group in phenylhydrazine can be expressed by the following arrangement:

CSalk.>CS>CO>COalk.

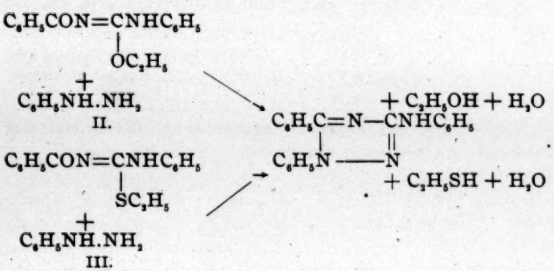
It seemed of interest to decide whether the above rule would hold in other types of compounds containing these groups, or whether it is a general tendency for 1,5-dialkyltriazoles to form in preference to the 1,3-dialkyltriazoles.

The acyloxygenpseudoureas—RCON=C(OR)NH$_2$—should yield 1,3-dialkyltriazoles according to the above representation, since water is represented as separating in preference to alcohol.

We find that the acyloxygenpseudoureas react less readily with phenylhydrazine than the other types of derivatives which have been examined. The acylpseudothioureas react at ordinary temperature with phenylhydrazine, while the

[1] Wheeler and Johnson: This Journal, 24, 198 (1900); Wheeler and Beardsley: *Ibid.*, 27, 258 (1902); 29, 74 (1903).

acyloxygenpseudoureas remain unaltered under the same conditions. They react smoothly, nevertheless, when heated to 130° to 150°, and give 1,5-dialkyltriazoles analogous to the acylpseudothioureas. The same triazole was obtained by heating phenylhydrazine with benzoylpseudoethylphenylurea as was obtained by Wheeler and Beardsley[1] from phenylhydrazine and benzoylthiolethylphenylpseudothiourea :



This behavior of the oxygenpseudoureas presents the first exception observed to the above rule. Apparently, from this there is a tendency for the 1,5-dialkyltriazoles to form rather than 1,3-dialkyltriazoles, and that the reaction does not necessarily proceed according to the above arrangement.

Wheeler and Beardsley[1] have prepared 1,3-diphenyl-5-mercaptotriazole by warming formylphenylhydrazine with benzoyl rhodanide and then treating the material with cold alkali. This reaction was not smooth and the triazole was always obtained mixed with secondary products.

We find that this triazole can be prepared very easily by combining benzoyl rhodanide with acetonephenylhydrazone. When the resulting semicarbazide was treated with dilute hydrochloric acid, or boiled with water, it was converted quantitatively into the 1,3-diphenyl-5-mercaptotriazole (Formula V.) :

[1] *Loc. cit.*

$$C_6H_5NH.N{=}C(CH_3)_2 + C_6H_5CONCS = C_6H_5N(C_6H_5CSNHCOC_6H_5)-N{=}C(CH_3)_2 \xrightarrow{\text{with HCl}} C_6H_5C(N{=}NC_6H_4){-}N{=}CSH$$

IV. V.

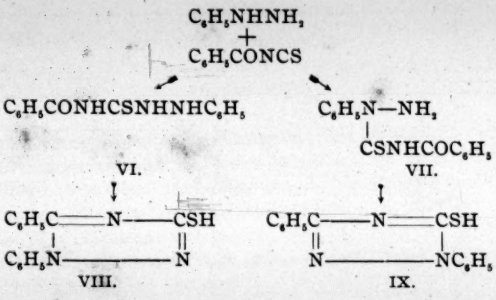
The behavior of the above semicarbazide (Formula IV.) towards hydrochloric acid and water is similar to an observation made by Arnold.[1] He found that cyanic acid readily combined with acetonephenylhydrazone to give the acetone derivative of unsymmetrical phenylsemicarbazide. When this acetone derivative was boiled with water it was converted into phenylsemicarbazide.

The behavior of the two above semicarbazides is in striking contrast to an earlier observation made by Vahle.[2] He showed that phenyl mustard-oil combined with acetonephenylhydrazone to form the acetone derivative of *a,b*-diphenylthiosemicarbazide. This compound was soluble in acids, and after prolonged boiling with strong hydrochloric acid could be precipitated unaltered from its acid solution.

Dixon[3] has investigated the action of phenylhydrazine on benzoyl rhodanide. He described the product formed as benzoylphenylthiosemicarbazide, and states that it does not melt at 220°.

We find that phenylhydrazine reacts with benzoyl rhodanide to form four definite products. Three of these we have been able to separate in a state of purity. Benzoylphenylthiosemicarbazide (Formula VI.) was isolated, which melted at 136° and not at 220°. Associated with the thiosemicarbazide was 1,5-diphenyl-3-mercaptotriazole (Formula VIII.), melting at 187°, and also 1,3-diphenyl-5-mercaptotriazole (Formula IX.), melting at 248°. We did not succeed in isolating the fourth product formed in this reaction (Formula VII.) :

[1] Ber. d. chem. Ges., **30**, 1016.
[2] *Ibid.*, **27**, 1514.
[3] J. Chem. Soc. (London), **55**, 304.



Benzoylphenylthiosemicarbazide (Formula VI.) was previously obtained in this laboratory[1] by treating ethyl benzoyldithiocarbamate with phenylhydrazine at ordinary temperature. It melted at 136° and agreed in none of its properties with Dixon's supposed thiosemicarbazide. When heated above its melting-point it was converted into 1,5-diphenyl-3-mercaptotriazole, melting at 187°.

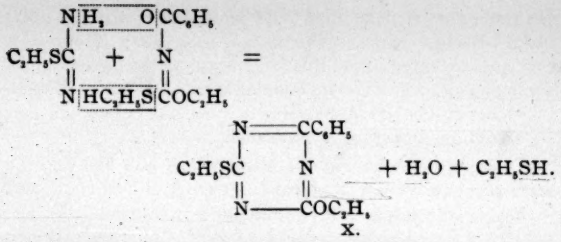
The formation of the two isomeric triazoles in the above reaction again show the strong tendency of phenylhydrazine to offer two points of attack towards reactive substances. The action of benzoyl rhodanide is perfectly analogous to the behavior of phenylhydrazine towards benzanilideimide chloride which was recently examined by Wheeler and Johnson.[2] This interesting behavior has also been observed by other investigators.[3]

The ease with which the acylimidothiocarbonates, RCON=C(OR)(SR), and acylimidodithiocarbonates, RCON=C(SR)$_2$, react with amines to form pseudoureas, suggested that they would react with the basic, non-substituted pseudothioureas to form triazine derivatives, as follows:

[1] Wheeler and Beardsley: *Loc. cit.*

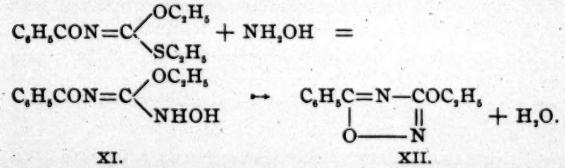
[2] This JOURNAL, **31**, 578.

[3] Busch: Ber. d. chem. Ges., **34**, 322; **36**, 3877; Frerich and Beckurts: Arch. Pharm., **237**, 346.



We find that pseudoethylthiourea combines with benzoylimidodiethylthiocarbonate at ordinary temperature. We were able to isolate a beautiful crystalline product melting at 48°. A nitrogen determination agreed with the calculated for ethylmercaptoethoxyphenyl-1,3,5-triazine (Formula X.).

One might expect hydroxylamine to react with an acylimidothiocarbonate to form a substituted acylpseudourea (Formula XI.), which could then condense to a furo-α,β'-diazole (Formula XII.) as follows:



We find that hydroxylamine reacts with benzoylimidodiethylthiocarbonate in alcoholic solution at ordinary temperature. Much heat was evolved, and mercaptan was given off immediately. We were able to isolate a product which melted at 48°, and a nitrogen determination agreed with the calculated for α'-phenyl-β-ethoxyfuro-α,β'-diazole (Formula XII.).

An isomeric oxyethylphenylfuro-α,β'-diazole has been prepared by Falck.[1] He obtained it by acting on the silver salt of α'-oxy-β-phenylfuro-α,β'-diazole with ethyl iodide at 100°.

[1] Ber. d. chem. Ges., 18, 2467; 19, 1481.

He states that it melts at 36°, but represents it with the alkyl group attached to nitrogen instead of oxygen. From work that has appeared from this laboratory[1] on the molecular rearrangement of imidoesters one might expect that a nitrogen alkyl derivative would be formed under the conditions that Falck obtained his furo-α,β'-diazole.

We have repeated Falck's experiments and find that the same ethyl derivative is formed when ethyl iodide is allowed to act on the silver salt at ordinary temperature. We feel justified in concluding from this result, and from previous work on the structure of silver salts and their behavior towards alkyl halides,[2] that the ethyl radical in Falck's furo-α,β'-diazole is attached to oxygen and not to nitrogen.

We also found that the acyloxygenpseudoureas react with great ease with hydroxylamine. Benzoylpseudoethylphenylurea and hydroxylamine reacted at once when heated in alcoholic solution to about 50°. A beautiful crystalline compound was formed, and a nitrogen determination agreed with the calculated for a furo-α,β'-diazole derivative. On account of lack of time the structure of these derivatives obtained with hydroxylamine must be decided at a later date.

Sell and Zierold[3] obtained the chloride of phenyl isocyanate by leading chlorine gas into a chloroform solution of phenyl mustard-oil. Nef[4] also obtained the same chloride by using phenyl isocyanate instead of phenyl mustard-oil.

We find that benzoyl rhodanide reacts as readily with chlorine gas as phenyl mustard-oil. The chloride is a light-yellow oil which can be distilled under diminished pressure without decomposition. It is a most intensely reactive body and combines with violence with water, alcohol, and amines. We expect to investigate some of the reactions of this interesting substance.

[1] Wheeler and Johnson: This JOURNAL, 21, 186; Wheeler: *Ibid.*, 23, 136.

[2] Nef: Ann. Chem. (Liebig), 266, 66; 276, 235. Tafel and Knoch: Ber. d. chem. Ges., 23, 104, 1550. Comstock and Kleeberg; This JOURNAL, 12, 493; Comstock and Wheeler: *Ibid.*, 13, 520. Stieglitz and Dains: J. Am. Chem. Soc., 21, 187: Wheeler and Johnson: This JOURNAL, 30, 32. Slimmer and Stieglitz: *Ibid.*, 31, 666.

[3] Ber. d. chem. Ges., 7, 1228.

[4] Ann. Chem. (Liebig), 270, 282.

EXPERIMENTAL PART.

The acyloxygenpseudoureas described in this paper were prepared by allowing amines to act on acylimidothiocarbonates at ordinary temperature. Certain representatives[1] of this class of derivatives have previously been described as oils. Recently Bruce[2] has prepared a series of these pseudoureas, which he has described as well-crystallized substances. The acyloxygenpseudoureas that we have prepared show little tendency to crystallize, small traces of impurity causing them to remain as oils for weeks. When obtained in a state of purity they form beautiful crystalline compounds, which are comparatively stable and can be recrystallized from the ordinary solvents.

Benzoylimidodimethylthiocarbonate, $C_6H_5CON=C\begin{matrix}OCH_3\\SCH_3\end{matrix}$.—This substance,[3] previously obtained as an oil, was prepared by dissolving methylbenzoylthioncarbamate and a molecular proportion of sodium ethylate in cold alcohol and then adding a molecular proportion of methyl iodide. We observed that the thiocarbonates were obtained much purer if the reaction was allowed to proceed at very low temperatures. It was separated from the alcohol by precipitating with water. It boiled at 200° at 20 mm. pressure. It solidified on cooling, and crystallized from ligroin in colorless prisms melting at 43°. A nitrogen determination gave:

	Calculated for $C_{10}H_{11}O_2NS$.	Found.
N	6.70	7.00

Benzoylpseudomethyl-m-nitrophenylurea,

$C_6H_5CON=C\begin{matrix}NHC_6H_4NO_2\\OCH_3\end{matrix}$.—This pseudourea[4] was previously obtained as an intermediate product in the preparation of benzoylnitrophenylurea from metanitroaniline and

[1] Wheeler and Johnson: This JOURNAL, 24, 190; McKee: *Ibid.*, 26, 209.
[2] J. Am. Chem. Soc., 26, 419.
[3] Wheeler and Johnson: This JOURNAL, 24, 190.
[4] *Loc. cit.*

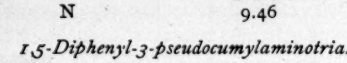
benzoylimidomethylthiolethylcarbonate. We have now isolated this pseudourea in a state of purity and find that it crystallizes from alcohol in needle-like prisms, and melts at 86° to 88°. A nitrogen determination gave :

	Calculated for $C_{18}H_{18}O_4N_2$.	Found.
N	14.05	14.20

Benzoylpseudomethylpseudocumylurea, $C_6H_5CON=C(NHC_6H_2(CH_3)_3)(OCH_3)$.—From pseudocumidine and benzoylimidomethylthiolethylcarbonate. It crystallized from alcohol in beautiful, needle-like prisms and melted at 87° to 89°. It was very soluble in ether and benzene. A nitrogen determination gave :

	Calculated for $C_{19}H_{20}O_2N_2$.	Found.
N	9.46	9.38

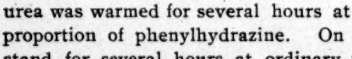
1,5-Diphenyl-3-pseudocumylaminotriazole,



.—This triazole was obtained when the above benzoylpseudomethylpseudocumylurea was warmed for several hours at 130° with a molecular proportion of phenylhydrazine. On allowing the melt to stand for several hours at ordinary temperature it finally solidified. The triazole crystallized from alcohol in rosettes of needle-like prisms and melted at 121° to 123°. A nitrogen determination gave :

	Calculated for $C_{23}H_{22}N_4$.	Found.
N	15.82	16.2

1,5-Diphenyl-3-phenylaminotriazole,



.—This was obtained by heating phenylhydrazine with benzoylpseudoethylphenylurea at 120° to 130°. It crystallized from alcohol in needles and melted at 202°. The triazole was previously obtained by Wheeler and

Beardsley[1] by treating benzoylphenylthiolethylpseudothiourea with phenylhydrazine. When their triazole was mixed with our triazole melting at 202° the melting-point was not lowered.

Benzoylpseudoethyl-m-nitrophenylurea, $C_6H_5CON=C\begin{matrix}NHC_6H_4NO_2\\OC_2H_5\end{matrix}$.—From metanitroaniline and benzoylimidodiethylthiocarbonate. After heating for a few hours at about 75° a thick oil was obtained which finally solidified. It crystallized from alcohol in the form of prisms and melted at 86° to 88°. A nitrogen determination gave:

	Calculated for $C_{18}H_{19}O_4N_3$.	Found.
N	13.4	13.31

Benzoylpseudoethyl-m-chlorphenylurea, $C_6H_5CON=C\begin{matrix}NH.C_6H_4Cl\\OC_2H_5\end{matrix}$.—From metachloraniline and benzoylimidodiethylthiocarbonate. After standing two weeks the pseudourea separated in the form of large prisms. It crystallized from alcohol in long, slender prisms and melted at 47° to 48°. A nitrogen determination gave:

	Calculated for $C_{18}H_{19}O_2N_3Cl$.	Found.
N	9.23	9.53

1,5-Diphenyl-3-m-chlorphenylaminotriazole, $C_6H_5C{=}N{-}CNHC_6H_4Cl$ (with C_6H_5N and N), was obtained by heating phenylhydrazine with benzoylpseudoethyl-*m*-chlorphenylurea at 120° to 130° for seven hours. The triazole crystallized after standing several hours at ordinary temperature. It crystallized from absolute alcohol in short, stout prisms, and melted at 195° to 196°. A nitrogen determination gave:

	Calculated for $C_{20}H_{15}N_4Cl$.	Found.
N	16.16	16.26

[1] *Loc. cit.*

Benzoylpseudoethylparatolylurea,

$C_6H_5CON=C\begin{matrix}NHC_6H_4CH_3\\OC_2H_5\end{matrix}$.—From paratoluidine and benzoylimidodiethylthiocarbonate. After standing two days the pseudourea crystallized in beautiful prisms. It separated from an alcoholic solution as an oil, and then crystallized in the form of long needles. It melted at 77° to 78°. A nitrogen determination gave:

	Calculated for $C_{17}H_{18}O_2N_2$.	Found.
N	9.93	10.4

1,5-Diphenyl-3-paratolylaminotriazole,

$C_6H_5C{=}N{-}CNHC_6H_4CH_3$ (with C_6H_5N bridging the two N atoms) .—This triazole was obtained by heating benzoylpseudoethylparatolylurea with phenylhydrazine. It crystallized from alcohol in minute, prismatic crystals, and melted at 227° to 228°. A nitrogen determination gave:

	Calculated for $C_{21}H_{18}N_4$.	Found.
N	17.17	17.07

This same triazole was first obtained by treating benzoylparatolylthiolethylpseudothiourea with phenylhydrazine.[1] Its structure was definitely established in a later paper by Wheeler and Beardsley.[2]

Benzoylpseudoethylparaanisylurea,

$C_6H_5CON=C\begin{matrix}NHC_6H_4.OCH_3\\OC_2H_5\end{matrix}$.—From paraanisidine and benzoylimidodiethylthiocarbonate. After standing for about one week the pseudourea was finally obtained in a crystalline form. It crystallized from alcohol in long, slender prisms, and melted at 66° to 67°. A nitrogen determination gave:

	Calculated for $C_{17}H_{18}O_3N_2$.	Found.
N	9.4	9.9

[1] Wheeler and Johnson: This JOURNAL, **26**, 414.

[2] *Loc. cit.*

1,5-Diphenyl-3-p-anisylaminotriazole, $C_6H_5C{=}N{-}CNHC_6H_4.OCH_3$ / $C_6H_5N{-}N$.—From benzoylpseudoethyl-*p*-anisylurea and phenylhydrazine. It crystallized from alcohol in rosettes of slender prisms, melting at 224° to 225°. A nitrogen determination gave :

	Calculated for $C_{21}H_{18}ON_4$.	Found.
N	16.3	15.7

Benzoylpseudoethylpseudocumylurea, $C_6H_5CON{=}C(NHC_6H_2(CH_3)_3)(OC_2H_5)$.—From pseudocumidine and benzoylimidodiethylthiocarbonate. After standing two days the pseudourea crystallized in magnificent prisms. It crystallized from alcohol in prisms and melted at 79° to 80°. A nitrogen determination gave :

	Calculated for $C_{19}H_{22}O_2N_2$.	Found.
N	9.03	9.03

Action of Benzoyl Rhodanide on Phenylhydrazine.

Eight grams of benzoyl rhodanide were dissolved in anhydrous ether and 5.3 grams of phenylhydrazine, mixed with ether, were slowly added through a dropping-funnel. A reaction took place at once and a beautiful, white, crystalline product separated from the ethereal solution. It crystallized from alcohol in the form of needles and prisms, and melted from 130° to 150°. The material behaved in every respect like a mixture.

The writer finally succeeded in purifying the material by repeated recrystallizations from alcohol. One product was isolated which was extremely soluble in alcohol and benzene. It separated in the form of needles and melted at 248°. It agreed in all its properties with 1,3-diphenyl-5-mercaptotriazole. Mixed with this triazole was another derivative which was somewhat less soluble in alcohol. By repeatedly crystallizing from alcohol it was obtained in a pure state and

melted constant at 187°. It had all the properties of 1,5-diphenyl-3-mercaptotriazole. When mixed with this triazole the melting-point was not lowered.

The alcoholic mother-liquors from the above crystallizations were combined and allowed to stand at ordinary temperature. After about twelve hours a large amount of crystalline material had separated. It crystallized from alcohol in prisms and melted at 136°. When this compound was mixed with benzoylphenylthiosemicarbazide (m. p. 136°) the melting-point was not lowered.

Acetone Derivative of a-Benzoyl-b-phenylthiosemicarbazide, $C_6H_5CONH.CSN(C_6H_5)N=C(CH_3)_2$.—This compound was prepared by mixing in anhydrous ether molecular proportions of benzoyl rhodanide and acetonephenylhydrazone. The ethereal solution was heated in the water-bath for about twenty minutes and then the ether was evaporated in a vacuum. The semicarbazide separated on the sides of the dish in the form of balls of minute prisms. It crystallized from alcohol in prisms and melted at 136°. A nitrogen determination gave:

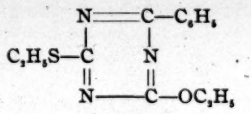
	Calculated for $C_{17}H_{17}ON_3S$.	Found.
N	13.50	13.25

When some of this semicarbazide was treated with hydrochloric acid it was immediately converted into 1,3-diphenyl-5-mercaptotriazole melting at 248°. This same transformation takes place on long boiling with water. Several attempts were made to isolate the intermediate *a*-benzoyl-*b*-phenylthiosemicarbazide by more mild hydrolysis, but mixtures were obtained of the triazole and unaltered semicarbazide.

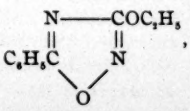
Condensation of Pseudoethylthiourea with Benzoylimidodiethylthiocarbonate.

Pseudoethylthiourea hydrobromide, $NH_2.C(SC_2H_5)=NH.HBr$, was dissolved in alcohol and combined with a molecular proportion of sodium ethylate. To this alcoholic solution of the free pseudothiourea was then added a molecular proportion of benzoylimidodiethylthiocarbonate. At first there was no apparent reaction, but after standing about one hour

mercaptan began to be given off freely. The mixture was allowed to stand at room temperature for about five days, when the excess of alcohol was evaporated on the steam-bath. We obtained a thick oil mixed with sodium bromide. The oil was taken up with ether to remove the sodium bromide, the ethereal solution dried over calcium chloride, and then the excess of ether evaporated in a vacuum. A beautiful crystalline deposit remained which showed signs of melting at 38°, and then melted to a turbid oil at 42° to 44°. The substance was extremely soluble in all the ordinary solvents. It crystallized from ligroin in prismatic crystals associated with some needles. When pure it crystallized from ligroin in well developed prisms, and melted at 47° to 48°. It was exceedingly stable, and after boiling with acids and alkalies it melted constantly at 47° to 48°. A nitrogen determination agreed with the calculated for ethylmercaptoethoxyphenyl-

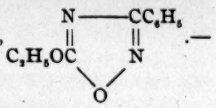
1,3,5-triazine, 

	Calculated for $C_{18}H_{18}ON_3S$.	Found.
N	16.09	16.41

α'-Phenyl-β-ethoxyfuro-α,β'-diazole,  ,

was obtained when an alcoholic solution of free hydroxylamine was united with a molecular proportion of benzoylimidodiethylthiocarbonate. Much heat was evolved and mercaptan was given off at once. After standing about eight hours the excess of alcohol was evaporated on the steam-bath. A beautiful crystalline deposit was formed, which was extremely soluble in ligroin, benzene, and ether. It crystallized from alcohol in stout prisms, and melted at 47° to 48°. A nitrogen determination gave :

	Calculated for $C_{10}H_{10}O_2N_2$.	Found.
N	14.72	15.2

α'-Ethoxy-β-phenylfuro-α,β'-diazole,  .—

This derivative has been described by Falck,[1] but he represents it as having the alkyl group joined to nitrogen instead of oxygen. We have made it by allowing ethyl iodide to act on the silver salt of α'-oxy-β-phenylfuro-α,β'-diazole[1] at ordinary temperature. It was obtained as an oil, which was finally made to solidify by washing with a little dilute sodium hydroxide solution. It crystallized from a mixture of benzene and ligroin in colorless needles, and melted sharply at 36°. It agreed in all its properties with Falck's description. A nitrogen determination gave :

	Calculated for $C_{10}H_{10}O_2N_2$.	Found.
N	14.72	14.77

Benzoylisocyanchloride, $C_6H_5CONCCl_2$.—This chloride was made by leading dry chlorine gas into a chloroform solution of benzoyl rhodanide. The reaction was apparently very smooth, and could be safely accelerated by gently warming the chloroform solution on the steam-bath while passing in the gas. The chloroform solution gradually changed in color, finally becoming dark-red, when the reaction was assumed complete. The mixture was distilled under diminished pressure. After removing the excess of chloroform and sulphur chloride the bulk of the remaining oil distilled between 140° to 148° at 31 to 32 mm. pressure. A fraction boiling constantly at 146° to 148° at 31 mm. was reserved for analysis. A chlorine determination gave :

	Calculated for $C_8H_5ONCl_2$.	Found.
Cl	35.14	35.11

[1] *Loc. cit.*

The oil is very sensitive towards moisture. It reacts with violence with alcohols and amines. The oil has a very penetrating odor and attacks the eyes.

NEW HAVEN, CONN., June 9, 1904.

ON THE FATE OF POTASSIUM MYRONATE IN THE ANIMAL ORGANISM AND ITS HYDROLYSIS BY THE FERMENTS OF THE LIVER.

BY J. H. KASTLE AND ELOISE CHESLEY MCCAW.

Several years ago Kastle and Johnston made a comparative study of the distribution of emulsin and myrosin in the vegetable kingdom. It was found that the tissue and aqueous extracts of nearly every plant examined possessed the power to hydrolyze amygdalin, whereas myrosin seemed to be confined to a comparatively few orders of plants. It is known further that emulsin occurs in the animal organism. Such being the case, it occurred to us that it might prove of interest to study the fate of potassium myronate in the animal organism and to determine whether this glucoside could be hydrolyzed by ferments of animal origin.

Accordingly, 5 cc. of a solution of pure potassium myronate, containing 0.5 gram of the glucoside, were injected subcutaneously into a young Belgian hare, of about 1 kilogram weight. Immediately after the injection the animal was placed in a cage, so arranged that the urine could be collected. The animal received no food of any kind during the period of experimentation. No ill effects resulted from the injection of this quantity of the glucoside. In about three and one-half hours after the injection the animal passed urine, which was collected and tested for potassium myronate in the following manner. Four tubes were prepared as follows:

1. Contained 2 cc. of the urine, 2 cc. of an extract of white mustard-seed, the activity of which towards potassium myronate had been previously tested, and which contained 1 per cent of sodium fluoride as antiseptic.

2. Contained 2 cc. of the urine and 2 cc. of the extract of white mustard-seed, without antiseptic.

3. Contained 2 cc. of the urine and 2 cc. of the extract of white mustard, which had been previously boiled, and no antiseptic.

4. Contained 2 cc. of water and 2 cc. of the extract of white mustard. These tubes were then kept in a water-bath at 40° C. for several hours. In tubes 1 and 2 the odor of mustard-oil was distinctly perceptible in three hours, whereas in tubes 3 and 4 the odor of mustard-oil failed to develop even after a much longer interval. The urine failed to reduce Fehling's solution, whereas after standing for some time with the active extract of white mustard-seed it gave an abundant reduction.

These results go to show that when injected subcutaneously some of the potassium myronate at least passes unchanged into the urine, and that like the majority, if not all, of the complex carbohydrates and glucosides it is not directly assimilable from the blood.

The attempt was then made to determine whether the glucoside could be assimilated by the animal, if administered by the mouth. Accordingly, on April 13th, the rabbit was given a breakfast of bread, and 2 cc. of a solution of potassium myronate, containing 0.5 gram of the glucoside, was administered by the mouth. Almost immediately the animal passed into a lethargic condition and continued to lose weight during the interval of the experiment, which lasted for several days. Ten minutes after the administration of the myronate the animal passed urine. This was tested for potassium myronate, by the method above described, with negative results. The animal passed urine a second time at the end of twenty-four hours. This specimen was also tested for myronate in the usual manner but also with entirely negative results. It was observed further that the urine did not reduce Fehling's solution either before or after treatment with the active extract of white mustard-seed. Still other specimens of urine obtained at later intervals were examined for potassium myronate with negative results. It would seem, therefore, that when taken by the mouth the potassium myronate is assimilated in the animal organism, and that it is

completely hydrolyzed at some point in the alimentary system.

The Hydrolysis of Potassium Myronate by the Ferments of the Liver.

The fact that the liver contains so many ferments and that it plays such an important part in processes of digestion and assimilation naturally suggested that possibly aqueous extracts of the liver might be found capable of hydrolyzing potassium myronate. In order to determine whether aqueous extracts of the liver could effect the hydrolysis of this compound, the following experiments were carried out: Five grams of the liver of the hog were thoroughly macerated by grinding in a mortar with fragments of glass. The mass was then intimately mixed with 50 cc. of water and strained through a muslin cloth. The conduct of this extract towards potassium myronate was then tested in the following manner:

Tubes were prepared containing equal amounts of a 1 per cent solution of potassium myronate and 5 cc. of the active and boiled extract of the liver, using in one experiment sodium fluoride and in another chloral as an antiseptic. The tubes were then heated to 40° C. in the water-bath for several hours. Those containing the active extract gave the odor of oil of mustard after several hours, whereas the control experiments gave no odor of this compound. These preliminary experiments seemed to indicate that the liver contains a ferment capable of hydrolyzing potassium myronate. On the other hand, the fact that such a small amount of the compound was hydrolyzed under these conditions would seem to show either that the liver contains only very small amounts of myrosin, or that the ferment could not be extracted from the liver cells by the method here employed. In order, therefore, to throw further light upon the subject the following experiments were carried out, using beef liver: One gram of liver was thoroughly macerated and intimately mixed in the porcelain mortar with 0.1 gram of potassium myronate. Five cc. of water were then rubbed into the mass and a small amount of sodium fluoride added. The mixture

was then placed in a test-tube and tightly corked. A second tube was prepared similar to the first, except that toluene was used as the antiseptic. These, together with a control experiment in which the liver employed had previously been heated to boiling, completed the series. The three tubes were then heated on the water-bath at 40° C. for three hours. The odor of mustard oil was very strong in the first tube and its contents were thickly coagulated, doubtless as the result of the action of the acid potassium sulphate resulting from the hydrolysis of the myronate. The odor of oil of mustard was fainter in the second tube, although still readily perceptible, and the clear filtrate therefrom was found to reduce Fehling's solution. The boiled control gave no odor of oil of mustard, and the filtrate therefrom did not reduce Fehling's solution. The results of these experiments left no room for doubt that the liver of the beef is capable of hydrolyzing potassium myronate. Similar experiments were carried out using the liver of other animals and other animal tissues with the following results:

Tissue employed.	Duration of experiment.	Results.
Liver of hog	24 hours	+
Pancreas of hog	"	—
Muscle of hog	"	—
Spleen of hog	"	—
Kidney of hog	"	—
Lung of hog	"	—
Mucous membrane of small intestine of hog	"	—
Liver of beef	3 hours	+
Liver of dog	21 hours	+
Spleen of dog	"	—
Kidney of dog	"	—
Mucous membrane of small intestine of dog	"	—
Liver of cat	2 hours	+
Liver of hen	24 hours	+
Liver of rabbit	1 hour	+
Liver of rat	24 hours	+
Liver of mouse	"	+
Liver of sheep	20 hours	+
Liver of frog	24 hours	+
Liver of fish	"	—

In the above table the sign + indicates that the odor of oil of mustard developed in the time indicated, whereas the sign — indicates that no odor of oil of mustard was perceptible.

It is evident from these results that the liver of all animals thus far investigated, with the exception of that of the fish, contains a ferment capable of effecting the hydrolysis of potassium myronate. It is interesting to note further that the liver seems to be the only source of animal myrosin.

Our results would seem to warrant the further conclusion that, like other complex carbohydrates and glucosides, potassium myronate is not directly assimilable from the blood, but that when administered by the mouth it is assimilated, probably through the agency of the liver. In certain of our experiments it has been observed that the solution reduced Fehling's solution before the odor of mustard was noticeable. This would seem to indicate that the hydrolysis of this glucoside by animal myrosin probably takes place in two stages, the first of which results in the splitting off of glucose, the second in the further breaking-down of the residue into oil of mustard and potassium acid sulphate.

STATE COLLEGE OF KENTUCKY.
LEXINGTON, June, 1904.

ON THE OXIDATION OF SULPHOCYANIC ACID AND ITS SALTS BY HYDROGEN PEROXIDE.

BY J. H. KASTLE AND CLAUDE ROBERT SMITH.

In the course of their study of the decomposition of hydrogen peroxide, Kastle and Loevenhart[1] observed that ammonium sulphocyanate is readily oxidized by hydrogen peroxide even in the cold and even in the absence of oxygen carriers, with the production of acid ammonium sulphate and hydrocyanic acid. It therefore occurred to one of us (Kastle) that it might prove of interest to study this oxidation somewhat more at length. A few preliminary experiments indicated that the reaction would lend itself to quantitative measurements. These were carried out by measuring the increase in the acidity of the solution. Since, however, it was desired to

[1] This JOURNAL, 29, 397, 563 (1903).

employ phenolphthalein as the indicator, ammonium sulphocyanate could not be used. With the metallic sulphocyanates, however, and with sulphocyanic acid itself, satisfactory measurements have been made by means of this indicator. Generally, the experiments were carried out in large test-tubes, in a total volume of 25 cc. In most of the experiments the total volume of 25 cc. consisted of 10 cc. of N/10 sulphocyanic acid or the sulphocyanate, 6 cc. of M/2 hydrogen peroxide, the theoretical amount, and 9 cc. of water.

The hydrogen peroxide was usually added last; the time of its addition served to mark the beginning of the experiment. At the end of certain intervals 5 cc. of the mixture were pipetted out and titrated with N/25 potassium hydroxide, using phenolphthalein as the indicator. The effect of various oxygen carriers on the progress of the oxidation, the effect of increasing amounts of hydrogen peroxide, the effect of temperature, and, finally, the order and velocity of the reaction have all been investigated. The results of these observations are given in the following pages.

On the Effect of Various Oxygen Carriers on the Progress of the Oxidation.

The influence of small amounts of the following substances on the progress of the oxidation has been studied: Manganese chloride, manganese dioxide, silver nitrate, potassium chloride, potassium bromide, potassium iodide, copper sulphate, copper nitrate, copper acetate, ferrous sulphate, mercuric chloride, and platinum black. Three series of experiments were carried out, one with potassium sulphocyanate, one with barium sulphocyanate, and one with sulphocyanic acid. In the experiments with platinum black and manganese dioxide 0.1 gram of each of these substances was employed. Equivalent quantities of the other substances were used, *viz.*, 2 cc. of a M/50 solution of each. The results of these experiments, together with all other necessary data, are given in Tables I., II., and III.

Table I.

Substances employed: 10 cc. N/10 potassium sulphocyanate; 2 cc. M/50 of the substance tested; 6 cc. M/2 hydrogen peroxide; 7 or 9. cc. water. Total volume of solution = 25 cc. Temperature, 20° C.

Cc. N/25 potassium hydroxide required.

Time in minutes.	Water.	Manganese chloride.	Silver nitrate.	Potassium chloride.	Potassium bromide.	Potassium iodide.	Copper nitrate.	Copper sulphate.	Nickel nitrate.	Nickel sulphate.	Cobalt nitrate.	Cobalt sulphate.	Ferrous sulphate.	Mercuric chloride.	Manganese dioxide.	Platinum black.
90	0.70	0.70	0.60	0.70	0.60	0.70	1.65	2.05	0.85	0.75	1.00	1.00	3.30	0.70	0.20	0.60
180	1.05	1.10	1.00	0.95	0.90	1.10	2.05	2.50	1.50	1.2	1.30	1.35	3.50	1.25	0.25	1.00
270	1.35	1.45	1.30	1.35	1.35	1.45	2.25	3.00	1.60	1.55	1.50	1.70	3.50	1.65	0.25	1.30
360	1.55	1.65	1.55	1.55	1.65	1.65	2.30	3.05	1.70	1.85	1.80	1.90	3.60	2.10	0.25	1.65
1360	2.30	2.45	2.30	2.30	2.40	2.20	2.55	3.25	2.40	2.30	2.45	2.55	3.60	3.00	0.25	2.15

Per cent of potassium sulphocyanate oxidized.

90	14.0	14.0	12.0	14.0	12.0	14.0	33.0	41.0	17.0	15.0	20.0	20.0	64.0	14.0	4.0	12.0
180	21.0	22.0	20.0	19.0	18.0	22.0	41.0	50.0	30.0	24.0	26.0	27.0	70.0	25.0	5.0	20.0
270	27.0	29.0	26.0	27.0	27.0	29.0	45.0	60.0	32.0	31.0	30.0	34.0	70.0	33.0	5.0	26.0
360	31.0	33.0	31.0	31.0	33.0	33.0	46.0	61.0	34.0	37.0	36.0	38.0	72.0	42.0	5.0	33.0
1360	46.0	49.0	46.0	46.0	48.0	44.0	51.0	65.0	48.0	46.0	49.0	51.0	72.0	60.0	5.0	43.0

Table II.

Substances employed: 10 cc. N/10 barium sulphocyanate; 2 cc. M/50 of the substance tested; 6 cc. M/2 hydrogen peroxide; 7 or 9 cc. of water. Total volume of solution = 25 cc. Temperature, 20° C.

Cc. N/25 potassium hydroxide required.

Time in minutes.	Water.	Manganese chloride.	Chrome alum.	Potassium chloride.	Potassium bromide.	Potassium iodide.	Copper nitrate.	Copper sulphate.	Nickel nitrate.	Nickel sulphate.	Cobalt nitrate.	Cobalt sulphate.	Ferrous sulphate.	Mercuric chloride.	Manganese dioxide.	Platinum black.
90	0.35	0.60	1.10	0.40	0.45	..	1.50	1.85	0.50	0.75	0.75	..	3.40	0.50	0.10	0.55
180	0.80	1.50	1.75	0.90	0.85	..	1.65	2.75	1.15	1.10	1.45	..	3.30	1.05	0.10	0.95
270	1.30	2.60	1.85	1.10	1.00	..	1.90	2.90	1.90	1.90	1.65	..	3.35	1.35	0.10	1.20
1360	1.90	2.70	2.50	1.85	1.85	..	2.15	2.90	2.00	2.00	2.60	..	3.30	2.00	0.10	1.75
Per cent of barium sulphocyanate oxidized.																
90	7.0	12.0	22.0	8.0	9.0	..	30.0	39.0	10.0	15.0	15.0	..	68.0	10.0	2.0	11.0
180	16.0	30.0	35.0	18.0	17.0	..	33.0	55.0	23.0	22.0	29.0	..	66.0	21.0	2.0	19.0
270	26.0	52.0	37.0	22.0	20.0	..	38.0	58.0	38.0	38.0	33.0	..	67.0	27.0	2.0	24.0
1360	38.0	54.0	50.0	37.0	37.0	..	43.0	58.0	40.0	40.0	52.0	..	66.0	40.0	2.0	35.0

Table III.

Substances employed: 10 cc. N/10 sulphocyanic acid; 2 cc. M/50 of the substance tested; 6 cc. M/2 hydrogen peroxide; 7 or 9 cc. of water. Total volume of solution = 25 cc. Temperature, 20° C.

Cc. N/25 potassium hydroxide required after deducting initial acidity of solution.

Time in minutes.	Water.	Manganese chloride.	Chrome alum.	Potassium chloride.	Potassium bromide.	Potassium iodide.	Copper nitrate.	Copper sulphate.	Nickel nitrate.	Cobalt nitrate.	Cobalt sulphate.	Ferrous sulphate.	Mercuric chloride.	Manganese dioxide.	Platinum black.
90	1.85	2.05	3.50	2.00	2.05	2.00	3.20	3.60	2.60	2.70	2.70	3.60	2.35	2.00	2.50
180	2.80	2.60	3.80	2.75	2.75	2.90	3.70	3.80	3.35	3.40	3.40	3.70	3.10	2.85	3.00
270	3.35	3.25	3.85	3.30	3.35	3.30	3.90	4.00	3.50	3.60	3.60	3.75	3 30	3.35	3.15
1140	3.45	3.35	3.95	3.45	3.40	3.50	3.90	4.10	3.65	4.00	4.00	3.75	3.70	3.35	3.25

Per cent of sulphocyanic acid oxidized.

90	37.0	41.0	70.0	40.0	41.0	40.0	64.0	72.0	52.0	54.0	54.0	72.0	47.0	40.0	50.0
180	56.0	52.0	76.0	55.0	55.0	58.0	74.0	76.0	67.0	68.0	68.0	74.0	62.0	57.0	60.0
270	67.0	65.0	77.0	66.0	67.0	66.0	78.0	80.0	70.0	72.0	72.0	75.0	66.0	67.0	63.0
1140	69.0	67.0	79.0	69.0	68.0	70.0	78.0	82.0	73.0	80.0	80.0	75.0	74.0	67.0	65.0

It is evident from these results that both in the presence of oxygen carriers and alone sulphocyanic acid is more rapidly oxidized by hydrogen peroxide than either of its salts. Secondly, that the oxidation both of the acid and the two sulphocyanates here employed is greatly accelerated by various substances, notably by those which have been found to effect the decomposition of hydrogen peroxide. Prominent among these are chrome alum, copper sulphate and nitrate, and ferrous sulphate. The salts of nickel and cobalt also accelerated the oxidation of the sulphocyanic acid, and to about the same extent each, whereas they exercised but little influence on the oxidation of the salts. Still another point of interest is that platinum black, manganese dioxide, and potassium iodide, all of which have been found to accelerate the oxidation of certain other substances by hydrogen peroxide, are in this case practically without influence on the rate of oxidation.

Determination of the Order and Velocity of the Reaction.

The oxidation of sulphocyanic acid by hydrogen peroxide is probably represented by the following equation:

$$HCNS + 3H_2O_2 = HCN + H_2SO_4 + 2H_2O.$$

If such is the case, the reaction in question is apparently of the fourth order. As but few reactions of high molecular order have ever been experimentally studied it occurred to us that it might prove of interest to determine the order of this reaction and also to determine the velocity of the reaction under different conditions.

Accordingly the order of the reaction was determined by van't Hoff's method, as follows: Two flasks, A and B, of 50 cc. and 100 cc. capacity, respectively, were prepared thus: A received 20 cc. N/10 sulphocyanic acid, 12 cc. M/2 hydrogen peroxide, and 18 cc. of water; B received the same amount of acid and peroxide, but the water added to it was 68 cc. These two flasks contained, therefore, the same amounts of reacting substances but in different concentrations, the concentration of one being twice that of the other, the unit of volume being 50 cc. These were allowed to remain

for thirty minutes at ordinary temperature, care being taken that both were under the same conditions. At the end of this time 10 cc. were pipetted out from the 50 cc. flask and titrated with N/25 potassium hydroxide. It required 14.15 cc., subtracting the initial acidity, equivalent to 10.12 cc. of N/25 potassium hydroxide; the amount of acid formed was equal to 4.03 cc., and the total acidity five times that amount; namely, 20.15 cc. We may tabulate these results, therefore, as follows:

Time in minutes.	Concentration.
0	50.00
30	29.85
Mean concentration,	39.925

Twenty cc. from the second flask, at the end of thirty minutes, required 11.50 cc. N/25 potassium hydroxide, that is, the acid formed was equivalent to 1.38 of N/25 potassium hydroxide, and hence the total acid generated was equivalent to five times that amount; namely, 6.9 cc.

Hence in the unit of volume at the second concentration the acid formed was equivalent to 3.45 cc. N/25 potassium hydroxide. These results, therefore, may be tabulated as follows:

Time in minutes.	Concentration.
0	25.00
30	21.65
Mean concentration,	23.275

Substituting these several values in van 't Hoff's equation, we arrive at the number representing the order of the reaction under consideration:

$$n = \frac{\log \left(\frac{dC_1}{dt} : \frac{dC_2}{dt}\right)}{\log (C_1 : C_2)} = \log \frac{\frac{dC_1}{dt} - \log \frac{dC_2}{dt}}{\log C_1 - \log C_2}.$$

$$\frac{dC_1}{dt} = \frac{50 - 29.85}{30} = 0.6716; \quad C_1 = 39.925.$$

$$\frac{dC_2}{dt} = \frac{25 - 21.55}{30} = 0.115; \quad C_2 = 23.275.$$

$\log_e 0.6716 = -0.3981$; $\log_e 0.115 = -8.21626$.

$\log_e 39.925 = 3.6870$; $\log_e 23.275 = 3.1474$.

Therefore,

$$n = \frac{-0.3981 - (-2.1626)}{3.6870 - 3.1474} = \frac{1.7645}{0.5396} = 3.27.$$

It would seem reasonable to conclude, therefore, that the change under investigation is one of the third order. Looked at from this standpoint, the oxidation of sulphocyanic acid by hydrogen peroxide probably takes place in two entirely distinct and independent stages, the first of which leads to the production of hydrocyanic acid and sulphur dioxide, the second involving the further oxidation of the sulphur dioxide to sulphuric acid. Thus we would have :

$$HCNS + 2H_2O_2 = HCN + 2H_2O + SO_3 ;$$

and $$SO_3 + H_2O_2 = H_2SO_4.$$

It is known that the oxidation of aqueous solutions of sulphur dioxide by hydrogen peroxide takes place with great rapidity at ordinary temperatures. Hence the amount of sulphuric acid formed in a given time would depend entirely on the amount of sulphur dioxide produced in the first phase of the oxidation. The first phase of the oxidation, however, is clearly a trimolecular process. These facts are in keeping with all that is generally known concerning the conduct of sulphur and its compounds on oxidation, *viz.*, that the formation of sulphur dioxide always marks the first phase of such processes.

With the view of determining the velocity constant of the reaction the following experiments were carried out :

Two flasks, A and B, were prepared, each containing 40 cc. of N/10 sulphocyanic acid, 24 cc. of M/2 hydrogen peroxide, and 36 cc. of water. These flasks were allowed to stand at room temperature, 17°.5 C. At the end of certain intervals 20 cc. of the mixture were withdrawn from the flask by means of a pipette and titrated with N/25 potassium hydroxide. After making the necessary allowance for the initial acidity of the mixture the following results were obtained :

Time in minutes.	Volume N/25 KOH required. A. cc.	B. cc.	C. A.	B.
30	3.69	3.79	0.0000009260	0.0000009260
60	5.99	5.99	0.0000009642	0.0000009642
90	7.79	7.94	0.0000010537	0.0000010970
120	8.99	9.09	0.0000010901	0.0000011940
150	10.09	10.24	0.0000011073	0.0000011519

The several values of C are calculated according to the equation for a reaction of the third order, $C = \frac{1}{x} \cdot \frac{x(2A-x)}{2A(A-x)}$.

It will be observed that in this series of experiments the velocity of the reaction slightly increases as the reaction proceeds. It was thought perhaps that this slight increase might be due to a slight rise of temperature during the progress of the experiment. It seemed desirable, therefore, to conduct a series of experiments at a perfectly constant temperature. Accordingly, two flasks were prepared, each containing 40 cc. N/10 sulphocyanic acid, 24 cc. M/2 hydrogen peroxide, and 36 cc. of water. During the interval of experimentation the flasks were kept in a bath of cracked ice. At the end of certain intervals 20 cc. of the solution were withdrawn from the flask by means of a pipette and titrated with N/25 potassium hydroxide. The results of this series of measurements are given in the table below, correction being made for the initial acidity of the solution.

Time in minutes.	Volume N/25 KOH required. A. cc.	B. cc.	C. A.	B.
30	1.24	1.24	0.0000002494	0.0000002494
60	2.19	2.19	0.0000002389	0.0000002389
90	3.09	3.09	0.0000002441	0.0000002441
120	3.99	3.99	0.0000002581	0.0000002581
			Average,	0.0000002476

A similar series of experiments with potassium sulphocyanate at 17°.5 C. gave the following results:

Time in minutes.	Volume N/25 KOH required. A. cc.	B. cc.	C. A.	B.
30	0.61	0.61	0.0000001065	0.0000001065
60	1.11	1.11	0.0000001008	0.0000001008
90	1.61	1.61	0.0000001015	0.0000001015
120	2.06	2.11	0.0000001012	0.0000001042
150	2.51	2.51	0.0000001021	0.0000001021
		Average,	0.0000001024	0.0000001030

We see thus that in the process under consideration it is possible to obtain fairly constant values for the coefficient of velocity of a reaction of the third order.

Finally, it has been observed that a rise of temperature of 10° C. nearly doubles the velocity of the reaction. That such is the case may be seen from the following:

Time in minutes.	Velocity constant at 0° C.	Velocity constant at 10° C.
30	0.0000002494	0.0000004649
60	0.0000002389	0.0000004633
Average,	0.0000024415	0.0000004641
Ratio of velocities at T and (T + 10)		1.90

This is in accord with the generalizations of van 't Hoff respecting the influence of temperature on chemical change.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, June, 1904.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

VII.—THE PREPARATION OF AROMATIC NITROSO COMPOUNDS.

BY FREDERICK J. ALWAY.

Up to the present time there has been developed no method of general application for the preparation of those aromatic nitroso compounds in which the nitrogen is attached to a carbon atom and of which nitrosobenzene is the simplest example. While, within recent years, a large number of the nitroso compounds has been prepared, the fact that such comparatively simple compounds as *m*-nitrosobenzoic acid and *p*-nitrosobenzoic acid have not hitherto been obtained, indicates the

want of some general method of procedure. Nearly all the nitroso compounds at present known are readily volatile with steam and, so, are easily separated from other compounds formed at the same time. The method that has been used in preparing most of the members of this class is that of Bamberger,[1] which consists in the oxidation of the β-alphylhydroxylamines obtained by the action of zinc dust and an ammonium salt solution upon the corresponding nitro compounds. When the resulting substance was not the pure nitroso compound, distillation with steam was used. The oxidation of amido compounds by means of Caro's reagent[2] has also been used by Bamberger[3] and to a limited extent by others[4] in the preparation of the same class of substances. The bright-green color of all nitroso compounds in solution and the characteristic odor of most of them made them easy of recognition. *o*-Nitrosobenzoic acid, which is not volatile with steam, has been prepared by E. Fischer[5] by the oxidation of the phenyloxindol obtained from benzoinoxime, using potassium permanganate as an oxidizing agent, and by Ciamician and Silber[6] by allowing solutions of *o*-nitrobenzaldehyde to stand exposed to the sunlight. The reaction in the latter case takes place according to the following equation:

$$O_2N.C_6H_4.CHO \longrightarrow ON.C_6H_4.CO.OH.$$

Similarly, Sachs and Kempf[7] have obtained *p*-chlor-*o*-nitrosobenzoic acid from the corresponding *p*-chlor-*o*-nitrobenzaldehyde.

In a former publication[8] I have pointed out that *p*-nitrosobenzaldehyde, while readily volatile with steam when freshly prepared by oxidizing *p*-hydroxylaminobenzaldehyde, is not volatile after it has been preserved for some time. It can, however, be changed back into the volatile form by fusion or

[1] Ber. d. chem. Ges., **28**, 245, 1218 (1895).
[2] Chem. Centrbl., II., 190 (1899).
[3] Ber. d. chem. Ges., **36**, 3803 (1903).
[4] *Ibid.*, **35**, 3034 (1902).
[5] *Ibid.*, **29**, 2064 (1896).
[6] *Ibid.*, **34**, 2040 (1901); **35**, 1080, 1897, 3596 (1902).
[7] *Ibid.*, **36**, 3302 (1903).
[8] J. Am. Chem. Soc., **24**, 1059 (1902).

by solution in alcohol or in acetic acid. Later,[1] I found that when zinc dust was added to the alcoholic solution of *p*-nitrobenzaldehyde containing acetic acid the zinc dissolved rapidly until the amount approximately corresponding to the equation

$$O_2N.C_6H_4.CHO + 2Zn + 4C_2H_4O_2 = HO.NH.C_6H_4.CHO + H_2O + 2Zn(C_2H_3O_2)_2$$

had disappeared, the solution assuming an orange color. The further addition of zinc produced no change. Zinc and acetic acid acted similarly upon other nitro compounds, including the nitrobenzoic acids as well as those nitro compounds from which nitroso compounds had been prepared. While the reduction-products of the latter gave, upon oxidation and distillation with steam, green distillates, the former gave colorless distillates. As, in most cases, the nitroso compounds were more readily volatile with steam than the corresponding nitro compounds, and as the nitrobenzoic acids were not volatile with steam, an investigation of the possibility of preparing nitroso compounds from non-volatile nitro compounds was undertaken in this laboratory. With the exception of *o*-nitrobenzoic acid and *o*-nitrocinnamic acid, all the nitro compounds so far worked with have given nitroso compounds. Farther, as in the case of *p*-nitrosobenzaldehyde, *m*-nitrosobenzaldehyde, and the nitrosobenzoic esters the corresponding azoxy compounds were formed at the same time by the oxidation of the *β*-hydroxylamines, it seemed probable that the oxidation-product of the substances obtained by the action of zinc dust and acetic acid upon the nitro acids was chiefly a mixture of nitroso and azoxy acids. Following this hypothesis four non-volatile nitroso acids have been isolated in this laboratory, *viz.*, *m*-nitrosobenzoic acid, *p*-nitrosobenzoic acid, *m*-nitrosocinnamic acid, and *p*-nitrosocinnamic acid. The phenomena observed upon the oxidation of the *o*-hydroxylamino acids were quite different from those observed in the other cases. No attempt was made to isolate any of the hydroxylamino compounds except that obtained from *p*-nitrobenzaldehyde.[2]

[1] Ber. d. chem. Ges., **36**, 793, 2303 (1903).
[2] J. Am. Chem. Soc., **24**, 1057 (1902).

The *m*- and *p*-nitrosobenzoic and the *m*- and *p*-nitrosocinnamic acids are not volatile with steam. They decompose without melting. *p*-Nitrosobenzoic acid and *p*-nitrosocinnamic acid pass more or less completely, on standing, into insoluble modifications. The latter dissolve, however, in hot sodium carbonate solution, from which they are precipitated by acids in a form soluble in ordinary solvents.

While all other nitroso compounds of this class are colorless or some shade of green or blue in the solid form, *p*-nitrosobenzoic acid and its esters, as well as *p*-nitrosocinnamic acid and its esters, *p*-nitrosobenzaldehyde and *p*-nitronitrosobenzene,[1] are yellow. All the yellow nitroso compounds, except the cinnamic series, form green solutions. The cinnamic compounds form yellowish-green or greenish-yellow solutions.

In view of the results already obtained, the following method is suggested as one likely to indicate the best means of obtaining any nitroso compound that has not hitherto been prepared: First, determine the volatility of the corresponding nitro compound. If it is volatile with steam reduce it in alcoholic solution by means of zinc dust and acetic acid. Treat the reduction-product with ferric chloride solution and subject the mixture at once to the action of steam. If the nitro compound is not volatile with steam proceed as above as far as the oxidation. Wash the oxidation-product well with water in order to remove as much as possible of the ferric chloride, as small quantities of ferric compounds hide the characteristic color of the nitroso compounds in solution. Extract the residue at once with a hot solvent. (Alcohol has proven the most satisfactory solvent in the reactions so far studied.) Repeated solution and reprecipitation may in some cases be found necessary in order to remove the ferric salts sufficiently to allow the characteristic color to appear. In some cases zinc dust and an ammonium salt solution may be found to give a better yield of the nitroso compound. Where it is preferable to prepare the nitroso compound from the amido compound the determination of the volatility of the nitro compound will indicate the method to be used in separa-

[1] Ber. d. chem. Ges., **36**, 3809 (1903).

ting the nitroso from the accompanying azoxy compound. Bamberger and Hübner[1] have shown that the two form at the same time when the amido compounds are oxidized by Caro's reagent.

A brief notice regarding the preparation of *m*- and *p*-nitrosobenzoic acids has already been published elsewhere.[2] Some modifications of the methods there outlined have since been found desirable.

EXPERIMENTAL.

p-Nitrosobenzoic Acid, $ON.C_6H_4.COOH$.—Five grams of *p*-nitrobenzoic acid were dissolved, by the aid of heat, in ordinary alcohol. This solution was rapidly cooled to the temperature of the room so that any acid that separated out might be in a fine state of division. After adding 10 cc. of glacial acetic acid and shaking the mixture well, 5 grams of zinc dust were added in small portions, with constant agitation. The mixture became warm, the greater part of the zinc dissolved, and the solution assumed an orange color. The crude reduction-product was poured into a cold 10 per cent ferric chloride solution and the mixture warmed to 45°. A yellow, flocculent precipitate formed. This was filtered out and washed thoroughly on the filter with water to remove as much as possible of the adhering ferric compounds. The moist residue was boiled with ordinary alcohol and the green alcoholic solution filtered from the dark colored residue. This extraction was repeated with fresh portions of alcohol until the filtrates ceased to be green. A gray, insoluble substance remained. When the oxidation-product was allowed to dry before treatment with hot alcohol the whole of it became insoluble. On standing, a yellow powder separated from the green solution.

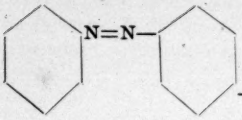
0.2830 gram substance gave 23.7 cc. moist N at 14° and 730 mm.

	Calculated for $C_7H_5O_3N$.	Found.
N	9.3	9.4

[1] Ber. d. chem. Ges., **36**, 3803 (1903).
[2] *Ibid.*, **37**, 333 (1904).

p-Nitrosobenzoic acid forms a yellow powder without distinct crystal form. It decomposes above 250° without melting. On drying, it becomes insoluble in ordinary solvents. A specimen that had been preserved five months was quite insoluble in boiling alcohol, acetic acid, and benzene; it dissolved in hot sodium carbonate solution with a yellowish-green color. This solution, when rendered acid, gave a yellow, amorphous precipitate, which, while still moist, dissolved in hot alcohol with a green color. *p*-Nitrosobenzoic acid dissolves in ammonia with a yellowish-green color. It is not volatile with steam. With aniline it condenses to benzene-*p*-azobenzoic acid.

Benzene-p-azobenzoic Acid,



.—*p*-Nitrosobenzoic acid was treated with an excess of aniline dissolved in glacial acetic acid and the mixture heated to boiling until the *p*-nitrosobenzoic acid had entirely dissolved. The reddish-brown solution thus obtained was cooled and then treated with dilute nitric acid. A reddish-brown precipitate formed. This was filtered out and twice recrystallized from alcohol. The acid formed orange crystals melting at 240° (uncorr.). The same acid had previously been prepared by other methods.[1]

m-Nitrosobenzoic Acid, $ON.C_6H_4.COOH$.—Five grams of *m*-nitrobenzoic acid, dissolved in 50 cc. of ordinary alcohol, were treated with 10 cc. of glacial acetic acid and then with 5 grams of zinc dust. The last was added in small portions with constant shaking. The mixture became warm, most of the zinc dissolved, and a clear light-yellow solution was formed. The unchanged zinc was filtered out and the filtrate poured into a 10 per cent solution of ferric chloride. A yellow solid rose to the surface of the mixture on standing. This was filtered out, washed on the filter with water, and

[1] Ber. d. chem. Ges., 19, 3023 (1886); Ann. Chem. (Liebig), 303, 384 (1881).

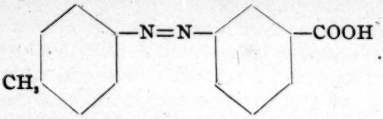
extracted with boiling alcohol, as described above in the case of the isomeric acid. There was thus obtained a brown solution, while a gray insoluble substance remained on the filter. The brown solution, when diluted with water and allowed to stand, gave a light-colored precipitate. The latter was washed with water repeatedly by decantation and finally on a suction-filter. On recrystallization from alcohol it formed a white solid without distinct crystal form.

0.1092 gram substance gave 9.1 cc. moist N at 14° and 723 mm.

	Calculated for $C_7H_5O_3N$.	Found.
N	9.3	9.3

m-Nitrosobenzoic acid, when heated, blackens at 230° without melting. It is not volatile with steam. It forms green solutions. With *p*-toluidine it forms *p*-toluene-*m*-azobenzoic acid.

p-Toluene-m-azobenzoic Acid,



. — A mixture of *m*-nitrosobenzoic acid, *p*-toluidine, and glacial acetic acid was heated to boiling for five minutes. The brown solution thus obtained was cooled and treated with dilute nitric acid. A brown solid separated out. This was filtered out and recrystallized from alcohol several times. The acid forms orange crystals melting at 192° (uncorr.). Löb[1] has obtained the same compound by the electrolytic reduction of a mixture of *p*-nitrotoluene and *m*-nitrobenzoic acid.

The gray residues obtained by extracting the *p*- and *m*-nitrosobenzoic acids from the oxidation-products were soluble in ammonia. The ammoniacal solutions, when rendered acid by the addition of mineral acids, gave light-colored precipitates. When the latter were filtered out and dried they were found to be insoluble in ordinary solvents, and when heated

[1] Ber. d. chem. Ges., 31, 2204 (1898).

they decomposed without melting. These properties, together with their method of formation, serve to identify them as the azoxy acids.[1]

o-Nitrobenzoic acid, when treated with zinc dust and acetic acid, gave a yellow solution. This reduction-product, when treated with ferric chloride solution, gave red or indigo-blue substances, according to the conditions of reaction. No nitroso compound was separated from these oxidation-products.

No attempt was made to isolate the hydroxylamino acids.

UNIVERSITY PLACE, NEBRASKA,
June 15, 1904.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

VIII.—THE NITROSOCINNAMIC ACIDS AND ESTERS.

BY FREDERICK J. ALWAY AND WALTER D. BONNER.

The volatility of the nitroso compounds is, in most cases, only slightly greater than that of the corresponding nitro compounds. *m*-Nitrocinnamic acid and *p*-nitrocinnamic acid are not volatile with steam, but their ethyl and methyl esters are volatile, though with difficulty. We have found that the nitroso compounds are very similar in their behavior toward steam to these nitro compounds. This fact renders their purification very difficult and the yields of pure substance extremely small. The para compounds are yellow, like the *p*-nitrosobenzoic compounds. The ethyl and methyl esters of *p*-nitrosocinnamic acid exist also in an instable, green modification. While *m*-nitrosocinnamic acid is colorless, its ethyl ester forms green crystals. Attempts to obtain *o*-nitrosocinnamic acid were unsuccessful. Evidently the corresponding azoxycinnamic acids are formed together with the *m*- and *p*-nitrosocinnamic acids.

EXPERIMENTAL.

p-Nitrocinnamic Acid, $O_2N.C_6H_4.CH:CH.COOH$.—This compound was prepared by heating, for eight hours, a mixture of 30 grams acetic anhydride, 22 grams of *p*-nitrobenzaldehyde, and 10 grams of powdered anhydrous sodium acetate.

[1] J. Chem. Soc. (London), 73, 146; Ann. Chem. (Liebig), 196, 18.

The flask containing this mixture was fitted with an air-condenser and heated in an oil-bath kept at a temperature of 180° by means of a thermoregulator. The reaction-product was distilled with steam until the odor of nitrotoluene could no longer be detected in the distillate. The crude *p*-nitrocinnamic acid was dissolved in sodium carbonate solution. After filtering this solution from any undissolved substance it was rendered acid by means of hydrochloric acid. The *p*-nitrocinnamic acid separated out in almost colorless, needle-shaped crystals. The yield was about 90 per cent of the theoretical amount.

p-Nitrosocinnamic Acid, $ON.C_6H_4.CH:CH.CO.OH$.—Two grams of finely divided *p*-nitrocinnamic acid were placed in a flask together with 4 cc. of glacial acetic acid and 50 cc. of alcohol. The contents of the flask were then well shaken and immediately treated with 2 grams of zinc dust. The mixture at once became green in color and warm. After ten minutes, during which the contents of the flask were kept well agitated, the unchanged zinc was filtered out and the clear, orange filtrate poured into a 10 per cent ferric chloride solution, which was kept at 40° to 60°. The yellow solid, that separated out, was filtered out, washed with water, and extracted with boiling alcohol, a brown, insoluble substance remaining on the filter. The alcoholic extract, which had a greenish-yellow color, deposited, on standing, a yellow solid. A further deposit was obtained by the addition of water to the filtrate from the first. The solid substance was brownish-yellow in color and a nitrogen determination showed that it was impure. The yield of crude acid was small and the loss attending each recrystallization was very large. After the third recrystallization from alcohol the substance was of a yellow color, with only a trace of brown. A nitrogen determination showed that it was still slightly impure.

0.2814 gram substance gave 19.2 cc. moist N at 23° and 730 mm.

	Calculated for $C_9H_7O_3N$.	Found.
N	7.9	7.4

By further recrystallization a small amount of the acid was obtained that had a pure yellow color, without a tint of brown. There was not enough of this pure acid, however, for an analysis.

p-Nitrosocinnamic acid forms a yellow powder of indistinctly crystalline form. It does not melt, but blackens when heated above 220°. When freshly prepared it is soluble in alcohol and in glacial acetic acid, giving yellowish-green or greenish-yellow solutions. After having been preserved in a dry state for several days a part of it was found to be insoluble in alcohol. This portion was found to dissolve readily in sodium carbonate solution with a yellowish-brown color. On acidifying this solution, a yellow precipitate was formed. The latter dissolved in hot alcohol with a greenish-yellow color.

Ethyl p-Nitrocinnamic Ester, $O_2N.C_6H_4.CH : CH.CO.OC_2H_5$. —This compound was prepared by heating 2 grams of *p*-nitrocinnamic acid with 20 cc. of absolute alcohol and 1 cc. of concentrated sulphuric acid, on the water-bath with return-condenser, for three hours. The reaction-mixture was cooled, treated with water, and then with an excess of sodium carbonate solution. The undissolved solid was filtered out and recrystallized from alcohol. The yield was almost quantitative. The ester crystallizes from alcohol in brown needles, melting at 137° (uncorr.). On being subjected to the action of steam the ester volatilizes slowly, collecting in the receiver as white needles, which melt at 141° to 142° (uncorr.). About 0.2 gram of ester was carried over by 1,000 grams of water vapor.

Ethyl p-Nitrosocinnamic Ester, $ON.C_6H_4.CH : CH : CO.OC_2H_5$.—Five grams of finely divided ethyl *p*-nitrocinnamic ester were treated with 75 cc. of alcohol and 12 cc. of glacial acetic acid. Zinc dust was then added in small quantities, with constant agitation, until the zinc was no longer dissolved. The mixture was then of an orange color. After standing ten minutes the reduction-product was poured, with constant stirring, into a 10 per cent ferric chloride solution. When the mixture was warmed, a yel-

low solid separated out. The crude oxidation-product was distilled with steam, a greenish-yellow liquid collecting in the receiver, while a brown solid remained in the distilling-flask. On standing over night yellow crystals separated from the distillate. The yield of nitroso compound varied from 10 to 15 per cent of the theoretical amount. It was found wasteful to place the reduction-product of more than 2 grams of the nitro compound in the distilling-flask at one time. Prolonged contact with boiling water seems to change the nitroso compounds into azoxy compounds.[1] After one recrystallization from aqueous alcohol the ester was pure.

0.1202 gram substance gave 8.1 cc. moist N at 23° and 724 mm.

	Calculated for $C_{11}H_{11}O_3N$.	Found.
N	6.8	7.2

Ethyl *p*-nitrosocinnamic ester forms yellow needles, which melt at 72° to 73° to a green liquid. It forms greenish-yellow solutions in alcohol, benzene, and acetic acid. On one occasion distinctly green crystals of the ester were obtained, but before they were dried they had changed to the yellow form, melting at 72° to 73°.

Methyl p-Nitrocinnamic Ester, $O_2N.C_6H_4.CH : CH.CO.OCH_3$.—This compound was prepared from *p*-nitrocinnamic acid and methyl alcohol by the same method as the ethyl ester. The yield was about 90 per cent of the theoretical amount. Like the ethyl ester, it volatilized very slowly in a current of steam, collecting in the receiver in the form of colorless crystals, melting at 160° (uncorr.).

Methyl p-Nitrosocinnamic Ester, $ON.C_6H_4.CH : CH.CO.OCH_3$.—One gram of the nitro ester was dissolved in boiling alcohol and treated with 2 cc. of glacial acetic acid. The hot solution was cooled under the tap so that the nitro ester would be in a fine state of division. Zinc dust was added to the mixture until, on warming gently, the zinc ceased to dissolve. The mixture became first green, then brown, and lastly yellow. It was then poured into fer-

[1] Ber. d. chem. Ges., 36, 3806 (1903).

ric chloride solution, which gave a yellow precipitate. On distilling the oxidation-product with steam a yellowish-green solution collected in the receiver while a brown solid remained in the distilling-flask. Lemon-yellow, needle-shaped crystals separated from the distillate. The melting-point of these crystals was not raised by recrystallization.

0.2040 gram substance gave 13.6 cc. moist N at 24° and 732 mm.

	Calculated for $C_{10}H_9O_2N$.	Found.
N	7.3	7.2

Methyl *p*-nitrosocinnamic ester forms lemon-yellow needles, melting at 111° to 112° (uncorr.) to a green liquid. The latter, on cooling, forms a green solid, which, on standing exposed to the sunlight a few days, changes to the yellow form. On several occasions green crystals collected in the condenser. After these had been dried in the dark they could be left exposed to the light for several days before passing into the yellow modification. When moist, green crystals were exposed to the sunlight they underwent the change within an hour. A specimen of the green form has been preserved in the dark for two months without showing any sign of change. The green crystals have the same melting-point as the yellow.

m-Nitrosocinnamic Acid, $ON.C_6H_4.CH:CH.CO.OH$.—Two grams of *m*-nitrocinnamic acid (Kahlbaum's preparation) were dissolved in 50 cc. of alcohol, treated with 4 cc. of glacial acetic acid, and then with 2 grams of zinc dust. The light-yellow solution thus obtained was filtered from the small amount of unchanged zinc. The filtrate, when poured into a 10 per cent ferric chloride solution, gave a flocculent, yellow precipitate. This was filtered out, washed well with water, and extracted with boiling alcohol. A brown solid remained undissolved. The green alcoholic solution, when treated with water and allowed to stand several hours, gave a flocculent white precipitate. The latter was filtered out and recrystallized from alcohol.

0.1722 gram substance gave 12.1 cc. moist N at 25° and 730 mm.

	Calculated for $C_9H_7O_3N$.	Found.
N	7.9	7.5

m-Nitrosocinnamic acid forms stellate groups of minute white needles, which turn slightly brown when allowed to stand exposed to the air in a moist condition. It forms green solutions and decomposes, without melting, at 230°.

Ethyl m-Nitrocinnamic Ester, $O_2N.C_6H_4.CH:CH.CO.OC_2H_5$. —This ester was prepared by boiling on the water-bath, for three hours, a mixture of 5 grams *m*-nitrocinnamic acid, 50 cc. ordinary alcohol, and 10 cc. concentrated sulphuric acid. The solution, after cooling, was diluted with water and the white solid so obtained washed on the filter with sodium carbonate solution. On recrystallizing from alcohol the ester was obtained in white needles, melting at 78° to 79° (uncorr.). It is slightly more volatile with steam than the isomeric para ester.

Ethyl m-Nitrosocinnamic Ester, $ON.C_6H_4.CH:CH.CO.OC_2H_5$.—Five grams of ethyl *m*-nitrocinnamic ester, dissolved in alcohol, were treated with 10 cc. glacial acetic acid and 3 grams of zinc dust, the latter being added in small portions. As the zinc dissolved the solution became warm and assumed a brownish-yellow color. The reduction-product was poured into a 10 per cent ferric chloride solution, a solid separating out almost immediately. The crude oxidation-product was at once distilled with steam. After the alcohol had passed over, the distillate became green and a few green crystals collected in the condenser. On standing, bright green crystals separated from the green distillate. The filtrate from these was colorless. Recrystallization from alcohol did not raise the melting-point of the crystals.

0.1904 gram substance gave 12.1 cc. moist N at 20° and 724 mm.

	Calculated for $C_{10}H_{11}O_3N$.	Found.
N	6.8	6.9

Ethyl *m*-nitrosocinnamic ester forms bright-green, rhombic

plates, readily soluble in alcohol, and melting at 65° to 66° (uncorr.). In solution and when melted it is green.

UNIVERSITY PLACE, NEBRASKA.,
June 15, 1904.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

IX.—ON CERTAIN NITROGEN COMPOUNDS.

BY FREDERICK J. ALWAY AND REUBEN M. PINCKNEY.

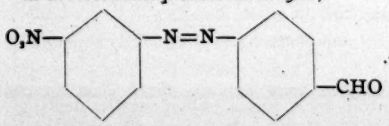
Nitroso compounds, under certain conditions, react almost quantitatively with amido compounds to produce azo compounds, according to the equation:

$$R.NO + H_2N.R' = R.N:N.R' + H_2O.$$

The most favorable conditions for this reaction seem to be those prevailing when a hot acetic acid solution of the nitroso compound is added to a boiling acetic acid solution of the amido compound. By slightly varying the conditions, it has been found, other reactions are induced. Thus, when a mixture of *p*-nitrosobenzaldehyde, *p*-toluidine, and glacial acetic acid is heated, a considerable quantity of *p*-azoxybenzaldehyde is formed.[1] We have found that *p*-nitrosobenzaldehyde condenses readily with *m*-nitraniline to produce the expected compound, *m*-nitrobenzene-*p*-azobenzaldehyde.

Ethyl *p*-nitrobenzoic ester, when treated with zinc and acetic acid, acts like the corresponding ethyl ester.[2] When the reduction-product is oxidized, ethyl *p*-azoxybenzoic ester is produced, together with ethyl *p*-nitrosobenzoic ester. The latter forms yellow crystals.

m-Nitrobenzene-p-azobenzaldehyde,



.—Two grams of *p*-nitrobenzaldehyde, dissolved in 25 cc. of glacial acetic acid, were slowly added to a boiling acetic acid solution of 4 grams

[1] Ber. d. chem. Ges., 36, 2310 (1903).
[2] *Ibid.*, 36, 2313 (1903).

of *m*-nitraniline. The mixture rapidly assumed a deep red color. It was kept hot for a few minutes and then allowed to cool slowly. Granular masses of crystals separated out. These were filtered out and washed on the filter with glacial acetic acid and with alcohol. The residue was transferred to a flask and covered with dilute nitric acid. After standing in contact with the nitric acid half an hour the solid was filtered out and washed with water. It was pure without further treatment.

	Calculated for $C_{13}H_9O_2N_3$.	Found.
N	16.5	16.8, 16.4, 16.4

m-Nitrobenzene-*p*-azobenzaldehyde forms granular masses, of indistinctly crystalline form and of orange-red color, melting at 223° (uncorr.). It is difficultly soluble in alcohol and in acetic acid.

Ethyl p-Nitrosobenzoic Ester, $ON.C_6H_4.CO.OC_2H_5$.—A solution of 5 grams of ethyl *p*-nitrobenzoic ester in 50 cc. of alcohol was treated with 10 cc. of glacial acetic acid and then with 4.5 grams of zinc dust. The last was added in small portions, the temperature of the mixture not being allowed to rise above 50°. The solution became brown, and on standing yellow crystals separated out. It was added to a mixture of 50 cc. of saturated potassium dichromate solution and 50 cc. of dilute sulphuric acid, a yellow precipitate being formed at once. The oxidation-product was distilled with steam. A green liquid collected in the receiver while a dark-colored, oily substance remained in the distilling-flask. Yellow crystals separated from the green distillate. These were twice recrystallized from alcohol.

	Calculated for $C_9H_9O_3N$.	Found.
N	7.8	7.7

Ethyl *p*-nitrosobenzoic ester forms yellow needles melting at 81° (uncorr.) to a green liquid. It forms green solutions.

Ethyl p-Azoxybenzoic Ester, $ON_2.(C_6H_4.CO.OC_2H_5)_2$.—The oily substance that remained in the distilling-flask in the preparation of the preceding compound solidified on cooling.

It was recrystallized from alcohol with the addition of charcoal. After the seventh recrystallization it consisted of orange leaflets, which melted to a turbid liquid at 113° (uncorr.). The latter became clear at 120° (uncorr.). This agrees with the observations of Meyer and Dahlem,[1] who obtained the same compound by the action of ethyl iodide upon the silver salt of *p*-azoxybenzoic acid. They obtained it in the form of yellow crystals. The orange color is probably due to traces of the red azo ester.

	Calculated for $C_{14}H_{18}O_5N_2$.	Found.
N	8.1	7.9, 8.0

UNIVERSITY PLACE, NEBRASKA,
June 15, 1904.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

X.—THE MOLECULAR WEIGHTS OF THE YELLOW NITROSO COMPOUNDS.

BY FREDERICK J. ALWAY AND ROSS A. GORTNER.

The nitroso compounds in which the nitroso group is attached to a carbon atom may be divided into three classes, according to the condition in which they exist in the solid form, *viz.*, (1) green or blue, (2) colorless or white, (3) yellow. It has been shown by Piloty,[2] Bamberger,[3] and Brühl[4] that the blue or green color depends upon the monomolecular condition, while the white or colorless form is evidence of the dimolecular condition. In an article by Alway and Bonner[5] it was shown that the only yellow nitroso compound known at that time, *p*-nitrosobenzaldehyde, possessed a normal molecular weight in solution in freezing acetic acid, in freezing benzene, and in boiling benzene. Since that time the methyl and ethyl esters of *p*-nitrosobenzoic acid[6] and of *p*-nitrosocinnamic acid,[7] as well as the acids themselves, have been ob-

[1] Ann. Chem. (Liebig), **326**, 337 (1903).
[2] Ber. d. chem. Ges., **35**, 3090, 3093, 3101 (1902).
[3] *Ibid.*, **33**, 3877 (1901).
[4] *Ibid.*, **31**, 1465 (1898).
[5] This JOURNAL, **30**, 111 (1903).
[6] Ber. d. chem. Ges., **36**, 2313 (1903).
[7] This JOURNAL, **32**, 394 (1904).

tained. All of these are yellow. We have determined the molecular weights of the four esters in freezing benzene. The acids, on account of the readiness with which they change into an insoluble form, are not well adapted to such determinations. The quantities of the *p*-nitrosocinnamic esters available for use were so small that the results in the case of these cannot be considered conclusive.

The *p*-nitrosobenzoic esters showed the normal molecular weight. The one *p*-nitrosocinnamic ester, which formed a greenish-yellow solution, gave a depression of the freezing-point corresponding to 50 per cent in the monomolecular form and 50 per cent in the dimolecular condition. The other *p*-nitrosocinnamic ester, which formed a yellow solution, gave a depression corresponding to the dimolecular condition.

Ethyl *m*-nitrosobenzoic ester, which we prepared for comparison with the corresponding methyl ester,[1] and which forms colorless crystals, exists in solution chiefly in the monomolecular condition. A small amount was present in the dimolecular condition at the temperature of freezing benzene.

In Experiments 1, 2, 3, 4, 5, and 6 the solutions were green and the color was not affected by changes of temperature. In Experiments 7 and 8 the solutions were green, but as the temperature fell the color diminished in intensity; on warming, the original intensity was restored. In Experiment 10 the solution was yellowish-green in color and no change was observed on lowering the temperature. In Experiment 9 the solution was yellow, without a distinctly green shade.

All the benzene solutions of the *m*- and *p*-nitrosobenzoic esters had changed to a red color after having stood several weeks in a dimly lighted room.

Ethyl m-Nitrosobenzoic Ester, $ON.C_6H_4.CO.OC_2H_5$.—Five grams of ethyl *m*-nitrobenzoic ester, dissolved in 50 cc. of alcohol, were treated with 10 cc. of glacial acetic acid and then with 5 grams of zinc dust, the latter being added in small portions and the mixture being kept well agitated. The yellow solution thus obtained was treated with ferric chloride solution and distilled with steam. A green liquid

[1] Ber. d. chem. Ges., 36, 2313 (1903).

Experiment No.	Dissolved substance.	Weight of solvent in grams.	Weight of dissolved substance in grams.	Percentage strength of solution.	Depression of freezing-point.	Theoretical molecular weight.	Molecular weight found.
1	Methyl *p*-nitrosobenzoic ester	21.3980	0.1414	0.66	0°.215	165	153.0
2	" " "	"	0.2737	1.28	0°.430	"	149.0
3	" " "	"	0.3681	1.72	0°.555	"	155.0
4	Ethyl " "	21.0980	0.2134	1.01	0°.290	179	174.0
5	" " "	"	0.3014	1.43	0°.400	"	179.0
6	" " "	"	0.3798	1.80	0°.480	"	187.0
7	" *m*-nitrosobenzoic "	21.0526	0.1238	0.59	0°.145	"	199.0
8	" " "	"	0.2344	1.29	0°.285	"	227.0
9	Methyl *p*-nitrosocinnamic ester	21.7854	0.0772	0.35	0°.035	191	490.0
10	Ethyl "	21.3498	0.0956	0.45	0°.075	205	300.0

collected in the receiver. This, on standing, deposited white crystals, which were recrystallized from aqueous alcohol.

	Calculated for $C_9H_9O_4N$.	Found.
N	7.8	7.8

Ethyl *m*-nitrosobenzoic ester forms stellate groups of white crystals, which melt at 52° to 53° to a green liquid.

A brown substance, probably the azoxy ester, remained in the distilling-flask.

UNIVERSITY PLACE, NEBRASKA,
June 17, 1904.

REVIEWS.

THE OCCURRENCE OF ALUMINIUM IN VEGETABLE PRODUCTS, ANIMAL PRODUCTS, AND NATURAL WATERS. A Contribution to the Bibliography of the Subject. By C. F. LANGWORTHY, PH.D., and PETER T. AUSTEN, PH.D. First edition, first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904.

"The material included in this contribution to the bibliography of aluminium deals only with the occurrence of this element in vegetable products, animal products, natural waters, and a few miscellaneous materials, such as edible earths. The general purpose has been to include only reference to such articles as report separate determinations of aluminium or some of its salts, and to omit the very large number in which iron and aluminium are reported together. In a few cases analyses have been cited which report 'traces' of aluminium, but the bulk of this material also has been omitted." In the four chapters, each of which is devoted to the occurrence of this element in one of the general sources stated above, the names of the authors are arranged alphabetically. The brief abstracts, averaging from three to eight lines, give the literature references and the percentage of aluminium found in the different cases. There is no discussion of the results, but where it has been deemed advisable, parts of the original articles are quoted. There are also several tables showing the percentage of aluminium phosphate in flour and in bread, aluminium in grape-juice, in tobacco and many other plant products, in waters, etc. The use of the book is made more convenient by means of an excellent index of 36 pages. It would be well to have a competent botanist correct the scientific names of the plants when the next edition is issued. Perhaps the authors of the articles are responsible for the mistakes noticed.

C. E. W.

A METHOD FOR THE IDENTIFICATION OF PURE ORGANIC COMPOUNDS by a Systematic Analytical Procedure Based on Physical Properties and Chemical Reactions, Vol. I., containing classified descriptions of about 2,300 of the more important compounds of carbon with hydrogen and with hydrogen and oxygen. By SAMUEL PARSONS MULLIKEN, PH.D., Instructor in Organic Chemistry and Organic Analysis at the Massachusetts Institute of Technology, Boston, Mass. Large 8vo. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904. pp. xii + 264. Price, cloth $5.00.

In this book the author attempts to substitute a new method for the identification of pure organic compounds, based on physical properties and chemical reactions, for the one now generally used which he designates as the method of the empirical formula. At the present time the procedure is to analyze a substance and thus determine its percentage composition. The molecular weight is then determined or conjectured, and from these data the empirical formula is calculated. The properties of the substance are then compared with those of all the known compounds having this formula, and its identity is established. The new method proposes to make use of the more easily determined properties like qualitative elementary composition, color, melting-point, boiling-point, solubility, specific gravity, etc., for the purposes of identification. It rests upon a classification similar to that employed in botany. The compounds, or chemical "species," have been first grouped into "orders" on the basis of their qualitative elementary composition; then into "genera" (aldehydes, acids, phenols, etc.) usually on the basis of behavior in simple chemical tests; and finally, arranged within each genus according to the increasing value of some readily determined constant like the melting-point or boiling-point. The name of each species is followed in the tables by a brief specific characterization, enumerating some of the simpler properties of the substance that have genuine analytical significance, and then, whenever possible, by detailed directions for preliminary and corroborative tests which can be performed with small quantities of material.

The present volume takes up only the compounds of carbon with hydrogen and with hydrogen and oxygen, and, hence, the method is limited to comparatively few compounds. It is the intention of the author to extend the method to compounds containing nitrogen in a subsequent volume.

It is not to be denied that the method of combustion analysis is tedious and troublesome and requires a certain amount of skill on the part of the student using it and that chemists would hail a better method for the identification of organic compounds with delight. It seems to the reviewer, however,

very questionable whether this new method is better than the old way. Even after locating an organic compound by means of its physical properties and chemical reactions, according to the new method, would not a careful chemist prefer to make a combustion analysis of the substance in order to be sure that he was right? The writer of this review remembers that some time ago he obtained a substance which had the properties of phenol and gave the chemical reactions of that substance, but it did not have the characteristic odor, and he was not sure that the substance was phenol until an analysis and a molecular weight determination showed that it had the composition represented by the formula C_6H_6O.

An enormous amount of work has been devoted to the book by the author, his pupils, and friends, and many of the tests have been worked out in detail so that they may be performed by any student with a little care.

The book is, singularly, free from errors, is well printed and bound, and is provided with a very excellent index. It will no doubt prove of value in identifying unknown organic compounds in the laboratory. W. R. O.

QUANTITATIVE ANALYSIS FOR MINING ENGINEERS. By EDMUND H. MILLER, PH.D., Adjunct Professor of Analytical Chemistry and Assaying in Columbia University. New York: D. Van Nostrand Company. 1904. pp. vii + 137.

This book consists of a series of articles on analytical chemistry which have been reprinted from the *School of Mines Quarterly*, and represents the work required of the mining engineers in Columbia University. It is not stated whether the book is supposed to present a systematic course on quantitative analysis, and from the material and its arrangement one is left in doubt in regard to this point. The first methods given are the usual elementary determinations of water, the SO_4, Mg, and Al ions in simple salts, but immediately following this is a chapter on the proximate analysis of coal. Then follow the gravimetric and volumetric methods for iron in ferric alum, and afterwards the determination of silica, phosphorus, and sulphur in iron ores.

From the first chapters one would suppose the book to be an elementary treatise; from the subsequent chapters an advanced work, especially so since the volumetric determination of iron is introduced without any discussion of volumetric principles. The book seems, therefore, to be a discussion of methods rather than a guide.

The subsequent chapters give the various gravimetric and volumetric methods for the analysis of iron and steel, the

analysis of limestone, zinc in its ores, copper in ores and mattes, lead, antimony, and arsenic in ores, and the analysis of iron, manganese, lead, and copper slags, with a brief chapter on flue-gas analysis. Most of the methods are given with considerable detail and accuracy, but one receives a strong impression that the work is very uneven, and that much of it has been written hurriedly. In some places, particularly in the determination of carbon in steel, the directions are very meager, and the student is referred to other books for details. The processes for the various ores and slags are much better given, but throughout the book there is a lack of consecutive and logical statement of methods. The discussion of precautions and conditions, and the explanation of reactions, is well done and up to date. References to original articles are frequently given, and there is also an appendix of references, although we are sorry to see references in a few cases to translations rather than the original articles. The book is introduced by chapters on ionization and mass action, but this discussion is almost too brief and fragmentary to be of much use.

The relative size of the reading and advertising matter which the publishers have seen fit to insert is strongly suggestive of the 10-cent magazine. H. F.

THE ELECTRIC FURNACE. By HENRI MOISSAN. Authorized translation by VICTOR LENHER, PH.D., University of Wisconsin. Easton, Pa.: The Chemical Publishing Co. 1904. pp. 305.

A review of the French original of this book appeared in this JOURNAL in 1897.[1] Considering the lapse of time, it may be well to again call attention to the value of the book.

In 1892 Moissan constructed his little laboratory electric furnace, in which the heat of the arc was utilized, while the object heated was kept out of contact with the arc, thus entirely avoiding the electrical action of the arc while employing its thermal action; and also avoiding contamination by the vapor of carbon. With sufficient electrical current a temperature of 3500° can be obtained in a few minutes.

Using this furnace, Moissan and his pupils have done an immense amount of systematic work; indeed, the amount of accurate work is astounding if we recall the many important discoveries made by Moissan during this period which do not involve the use of the furnace; we need only refer to the hydrides of sodium and potassium, to the preparation of pure calcium, to the remarkable series of investigations at low temperatures.

[1] "Le Four Électrique," THIS JOURNAL, 19, 623.

Although the furnace is so simple that any one can make it, and although it and various modifications of it were quickly listed by dealers at low price, it is a curious fact that little accurate research work has been done with it outside of Moissan's laboratory. As a rule, an important new apparatus or a new reaction of general application is scarcely made public before it is seized on by a host of workers—for example, the "Grignard reaction." That Moissan has been practically allowed a monopoly of this research work gives the book reviewed its value. It is a broad but fair statement, that our knowledge of chemical action at high temperatures is mainly due to Henri Moissan, and is recorded in this volume, which is therefore unique; it is not a luxury nor a substitute for some other book on the subject, it is a necessity. A chemist who has not read it or the original papers in the *Comptes rendus*, does not know the properties of many of the pure metals, or of the different modifications of elementary carbon, or of the numerous carbides, borides, and silicides.

Attention was called in the previous review to the literary polish of the original. This is lacking in the translation, which is rough and occasionally obscure, but is literal, and has the advantage of additional matter bringing the work up to this year. E. R.

CHEMIE DER EIWEISSKÖRPER. Von DR. OTTO COHNHEIM, a. o. Professor der Physiologie an der Universität Heidelberg. Zweite vollständig neu bearbeitete Auflage. Braunschweig: Friedrich Vieweg und Sohn. 1904. pp. 315.

The appearance of the second edition of this remarkably complete and accurate book will be welcomed by all those who are interested in this subject. The great advance that has been made in the subject of proteid chemistry is made very apparent by comparing the second edition of this book with the first. The fundamental work of Hopkins and Cole, and of Fischer and his pupils, is treated of in detail. The literature up to January, 1904, is given. All who are interested in the subject of proteid chemistry should have access to this book. A. S. L.

GRUNDLINIEN DER ANORGANISCHEN CHEMIE. VON WILHELM OSTWALD. Zweite, verbesserte Auflage. Leipzig: Verlag von Wilhelm Engelmann. 1904.

The first edition of this book was reviewed in this JOURNAL at the time of its appearance three years ago. No essential changes have been made in the work in the preparation of this new edition. The introductory paragraphs have been reconstructed and the fundamental conceptions developed

more clearly and sharply. For the expression "normal weight," used in the first edition, the expression "molar weight" has been substituted in this. Is this not too much of a concession to the molecular hypothesis? Of the atomic hypothesis the author says: "Auch in diesem Buche soll von diesem allgemeinen Gebrauche nicht wesentlich abgewichen werden. Doch läge es sicher im Interesse der Wissenschaft, wenn in dieser Berichtung eine grössere Vorsicht beobachtet würde, und deshalb ist hier Wert darauf gelegt worden, die Ausdrucksformen der Atomhypothese so sparsam anzuwenden, als es der Sprachgebrauch nur gestattet."

Ostwald's book has undoubtedly been of great service in showing teachers of chemistry how their subject may be developed logically. In order that a reformer may be even partially successful, it seems necessary for him to be an extremist. Some of us may squirm as we read Ostwald, but no doubt we are helped unless we are past help. It is an advantage to have even a few of the scales removed from our eyes. We are all groping. It is to be hoped that we are moving in the direction of the light. I. R.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. XII. BAND. DIE ELEKTROCHEMISCHE INDUSTRIE DEUTSCHLANDS. Von P. FERCHLAND, DR. PHIL. Mit 4 Figuren und Tabellen im Text. Halle a. S. Verlag von Wilhelm Knapp 1904.

In the present number of this carefully prepared series of monographs the author gives an account of the historical development of electrochemical industries in Germany. In the 64 pages of the monograph are short chapters on the more important substances that are now prepared by electrical methods. Among other things, the way in which the water supply of cities can be purified by means of ozone, is described. This seems of especial interest in view of the copper sulphate method, which has come so prominently before the public in the last few months. There is an index of "persons and firms." C. E. W.

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